

FORM PTO-1390 (REV. 12-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 514453-3916
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known see 37 C.F.R. 1.5) 10/070242
INTERNATIONAL APPLICATION NO. PCT/EP00/08518	INTERNATIONAL FILING DATE 31 AUGUST 2000	PRIORITY DATE CLAIMED 01 SEPTEMBER 1999	
TITLE OF INVENTION FIVE MEMBERED-RING COMPOUNDS AND UTILIZATION THEREOF IN LIQUID CRYSTAL MIXTURES			
APPLICANT(S) FOR DO/EO/US Barbara HORNING, Toshiaki NONAKA, Ayako OGAWA, Wolfgang SCHMIDT, Rainer WINGEN			
<p>Applicants herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31). <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). <input type="checkbox"/> has been communicated by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <input checked="" type="checkbox"/> is attached hereto. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). <input type="checkbox"/> have been communicated by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input checked="" type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11 to 20 below concern document(s) or information included:</p> <ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). <input checked="" type="checkbox"/> Other items or information: <div style="margin-left: 20px;"> PCT/IB/304, PCT/IPEA/402, 409, 416 PCT/ISA/210, 1 page Abstract </div> 			

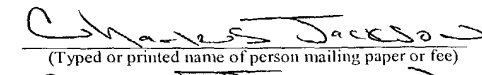
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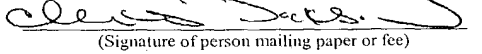
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U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) 10/070242		INTERNATIONAL APPLICATION NO. PCT/EP00/08518		ATTORNEY'S DOCKET NO. 514453-3916	
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21. <input checked="" type="checkbox"/> The following fees are submitted				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$1040.00 International preliminary examination fee (37 C.F.R. 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... \$740.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)..... \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total Claims	12 - 20 =	0	x \$18.00	\$ 0.00	
Independent Claims	3 - 3 =	0	x \$84.00	\$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00	
TOTAL OF ABOVE CALCULATIONS =				\$	
<input type="checkbox"/> Applicant claims small entity status. See 37 C.F.R. 1.27. The fees indicated above are reduced by 1/2.				+	
SUBTOTAL =				\$	
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TOTAL NATIONAL FEE =				\$	
Fee for recording the enclosed assignments (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				+	
TOTAL FEES ENCLOSED =				\$ 890.00	
				Amount to be refunded:	
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b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
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NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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 28,029
 REGISTRATION NUMBER

Dated: February 27, 2002

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CERTIFICATE OF MAILING – SEPARATE PAPER

Attorney Docket No. : 514453-3916
Serial No. : PCT/EP00/08518
Applicant(s) : Barbara Hornung et al.

Date of Deposit February 27, 2002 via "Express Mail" # EV 001581103US

I hereby certify that a PCT, a Fee Transmittal Sheet, and related documents for the above-referenced application are being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to:

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"as originally filed"

Five-membered ring compounds and their use in liquid-crystalline mixtures

5

Besides nematic and cholesteric liquid crystals, optically active, tilted smectic (ferroelectric) liquid crystals have also recently been used in commercial display
10 devices.

Clark and Lagerwall have been able to show that the use of ferroelectric liquid crystals (FLCs) in very thin cells results in opto-electrical switching or display elements which have response times which are of up to 1000 times faster than
15 conventional TN ("twisted nematic") cells (see, for example, EP-A 0 032 362). Owing to this and other favorable properties, for example the possibility of bistable switching and the virtually viewing angle-independent contrast, FLCs are basically highly suitable for areas of application such as computer displays.

20 For a more detailed discussion of the technical requirements of FLCs, reference is made to European Patent Application 97118671.3 and DE-A 197 48 432.

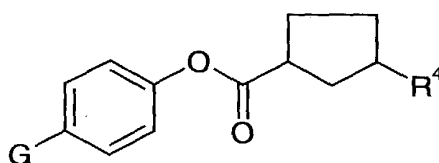
Thiophene derivatives have already been described for use in liquid-crystal mixtures, e.g. in EP-B 0 500 072. Some 3- or 4-fluorothiophenecarboxylic acids
25 have also been described, e.g. in Tetrahedron Letters 1997, 38(6), 1049; Heterocycles 23, 1431 (1985); Synth.Comm. 24, 95 (1994). However, these latter documents do not indicate any suitability for use as a building block for liquid crystals.

30 JP-A 6306098 describes esters of furanacrylic acid having terminally polar phenols for use in nematic liquid-crystal mixtures.

JP-A 10-333113 describes 3,5-diarylisoxazoles for use in ferroelectric liquid-crystal mixtures, especially operated in inverse mode.

2,5-Diarylthiazoles for use in ferroelectric liquid-crystal mixtures are described,
5 for example, in EP-B 0 439 170.

Cyclopentane derivatives have previously been described in general for use in liquid-crystal mixtures in US 4,873,019; however, this document does not suggest to the person skilled in the art that the compounds of the formula (II) encompassed
10 by the general formula of this document are particularly suitable as components of chiral smectic liquid-crystal mixtures.



(II)

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in which

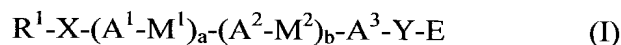
R⁴ is as defined below

G is F or CN or trans-4-propyl-cyclohexyl or trans-4-butyl-cyclohexyl or an alkyl radical of 1 to 15 carbon atoms, in which one or more nonadjacent CH₂ groups
20 may be replaced by -O-, -CO-, -OCO-, -O-CO-O-, -CHhalogen-, -CHCN- and / or -CH=CH-.

However, since the development, in particular of ferroelectric liquid-crystal mixtures, can in no way be regarded as complete, display manufacturers are
25 interested in a wide variety of components for mixtures, partly because only the interaction of the liquid-crystalline mixtures with the individual components of the display device or of the cells (for example the alignment layer) allows conclusions to be drawn on the quality of the liquid-crystalline mixtures.

It has now been found that five-membered ring compounds of the formula (I), even when admixed in small amounts, have a favorable effect on the properties of liquid-crystal mixtures, in particular chiral smectic mixtures, for example regarding the dielectric anisotropy and/or the melting point, but also regarding the switching behavior, the tilt angle values and the temperature dependence of the tilt angle.

The invention therefore provides five-membered ring compounds of the formula (I),



where the symbols and indices have the following meanings:

E is a radical $T-Z-R^2$ containing a five-membered ring, where:

- (i) **T** is undirected and is
4-fluorothiophene-2,5-diyl, 3-fluorothiophene-2,5-diyl,
3-fluorothiophene-2,4-diyl or 5-fluorothiophene-2,4-diyl
- Z** is a single bond or -O-
- R²** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that
- a) the -CH₂- group nearest to the thiophene cannot be replaced by -O- when Z is -O-
- b) R² can only be hydrogen when Z is a single bond,

- (ii) **T** is furan-2,5-diyl or furan-2,4-diyl
- Z** is a single bond or -O-

R² is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH₂ group nonadjacent to furan may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F,

(iii) **T** is undirected and is isoxazole-3,5-diyl
Z is a single bond or -O-

R² is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that

a) the -CH₂- group nearest to the isoxazole cannot be replaced by -O- when Z is -O-

b) **R²** can only be hydrogen when Z is a single bond,

(iv) **T** is undirected and is thiazole-2,5-diyl or thiazole-2,4-diyl
Z is a single bond
R² is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F,

(v) **T** is cyclopentane-1,3-diyl
Z is a single bond or -O-
R² is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or

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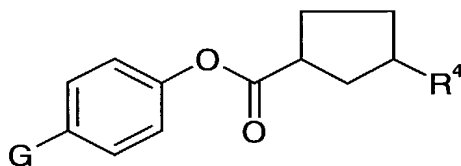
-OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that

a) the -CH₂- group nearest to the cyclopentane cannot be replaced by -O- when Z is -O-

5

b) R² can only be hydrogen when Z is a single bond,

with the exception of compounds of the formula (II)



(II)

10

in which

R⁴ is as defined for R²

G is trans-4-propyl-cyclohexyl or trans-4-butyl-cyclohexyl or an alkyl group of 1 to 15 carbon atoms, in which, in addition, one or more nonadjacent CH₂ groups may be replaced by -O-, -CO-, -OCO-, -O-CO-O-, -CHhalogen-, -CHCN- and/or -CH=CH- or is F, CN,

15

(vi) T is cyclopentane-1,3-diyl, in which one -CH₂CH₂- or -CH₂CH- group is replaced by a -CH=CH- or CH=C- group respectively

20

Z is a single bond

R² is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the proviso that the -CH₂- group nearest to the cyclopentene cannot be replaced and where

25

Y cannot be -CH₂-CH₂-,

R¹ is hydrogen or a straight-chain or branched C₁₋₂₀-alkyl or C₂₋₂₀-alkenyl radical (with or without asymmetric carbon atoms), where

- a) one or two nonterminal CH₂ groups may be replaced, independently of one another, by -O- or -C(=O)-, with the proviso that two adjacent CH₂ groups cannot be replaced in the same way, and/or
- b) one CH₂ group may be replaced by -C≡C-, and/or
- c) one CH₂ group may be replaced by -Si(CH₃)₂-, cyclopropane-1,2-diyl, cyclobutane-1,3-diyl, cyclopentane-1,4-diyl, bicyclo[1.1.1]pentane-1,3-diyl or cyclohexane-1,4-diyl, and/or
- d) one or more H atoms may be replaced by F and/or CN,
- e) in the case of a branched alkyl radical containing asymmetric carbon atoms, the asymmetric carbon atoms have -CH₃, -OCH₃, -CF₃, F, CN and/or Cl as substituents or are incorporated into a 3- to 7-membered ring, in which, in addition, one or two non-adjacent CH₂ groups may be replaced by -O- and one CH₂ group non-adjacent to these groups may be replaced by -OC(=O)-;

X is a single bond, -O-, OC(=O)-, -C(=O)O- or -OC(=O)O-

Y is -OC(=O)-, -OCH₂-, -CH₂CH₂-

A¹, A², A³ are each, independently of one another,

phenylene-1,4-diyl, unsubstituted or monosubstituted or disubstituted by CN or F, phenylene-1,3-diyl, unsubstituted or monosubstituted or disubstituted by CN or F, cyclohexane-1,4-diyl, in which one or two H atoms may be replaced by CN and/or CH₃ and/or F, 1-cyclohexene-1,4-diyl, in which one H atom may be replaced by F, 1-alkyl-1-silacyclohexane-1,4-diyl, pyridine-2,5-diyl, unsubstituted or monosubstituted by F, pyrimidine-2,5-diyl, unsubstituted or monosubstituted by F, cyclopentane-2,5-diyl or thiophene-2,5-diyl;

M^1 , M^2 are undirected and are each, independently of one another,

-OC(=O)-, -OCH₂-, -CH₂CH₂-, -OC(=O)CH₂CH₂-, -OCH₂CH₂CH₂-,
-C≡C-, -CH₂CH₂CH₂CH₂- or a single bond;

5 **a, b** are each, independently of one another, 0 or 1.

The term "terminal" means, for example in R^1 , the CH₂ groups connected to X or to H. The term "undirected" means that incorporation of the group in the form of its mirror image is possible.

10

The five-membered ring compounds of the formula (I) are fluorinated thiophene derivatives (i), furan derivatives (ii), isoxazole derivatives (iii), thiazole derivatives (iv), cyclopentane derivatives (v) or cyclopentene derivatives (vi).

15 In one embodiment of the invention, one or more of the following provisos apply:

For thiophene derivatives (i), A^1 , A^2 , A^3 are not cyclopentane-2,5-diyl.

For furan derivatives, A^1 , A^2 , A^3 are not cyclopentane-2,5-diyl.

For isoxazole derivatives, A^1 , A^2 , A^3 are not cyclopentane-2,5-diyl.

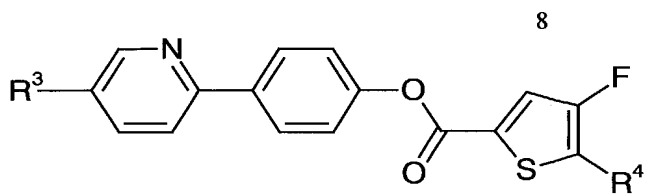
20 For thiazole derivatives, A^1 , A^2 , A^3 are not cyclopentane-2,5-diyl.

For cyclopentane derivatives, A^1 , A^2 , A^3 are not thiophene-2,5-diyl.

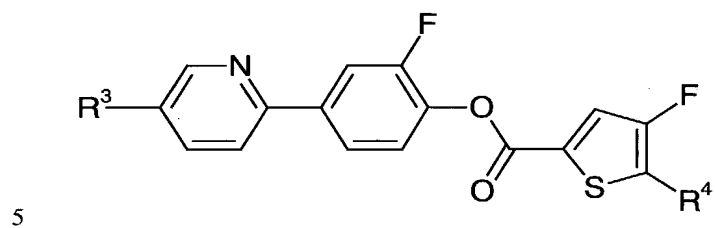
For cyclopentene derivatives, cyclopentane-1,4-diyl is replaced by cyclopentane-1,3-diyl for R^1 in proviso c).

25 **Fluorinated thiophene derivatives**

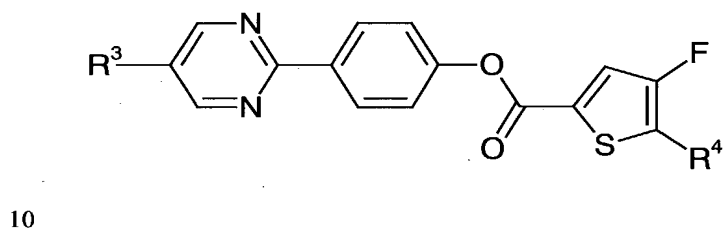
Preferred thiophene derivatives (i) are the following compounds of the formulae (I-1) to (I-33)



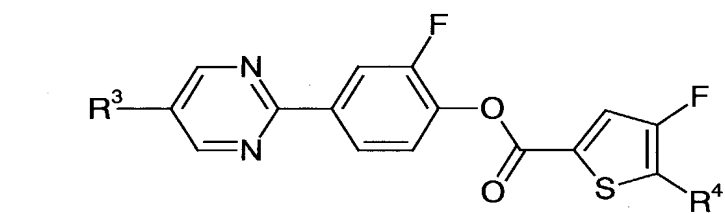
(I-1)



(I-2)

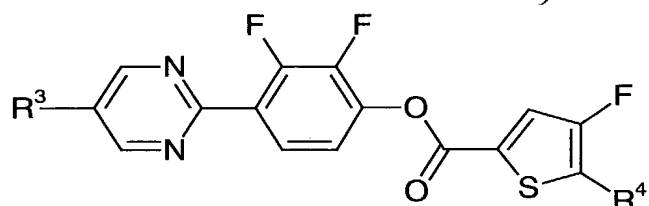


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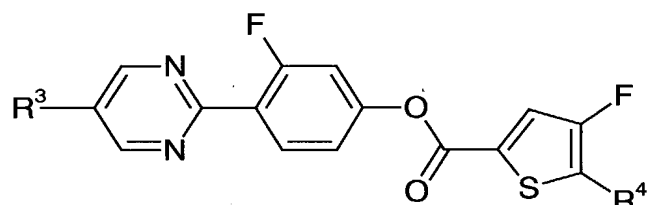
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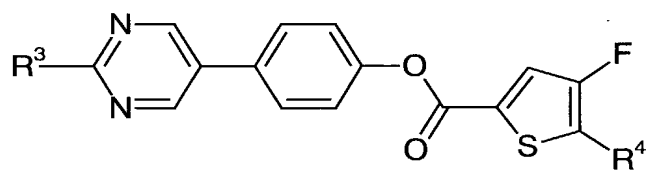
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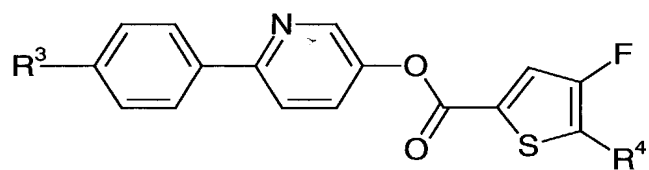
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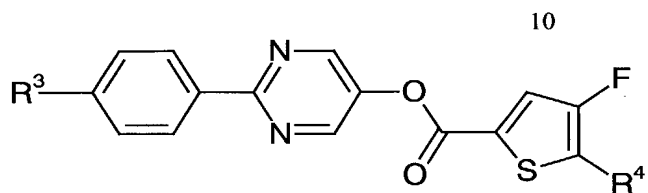


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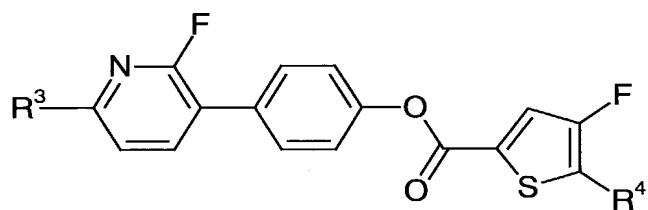
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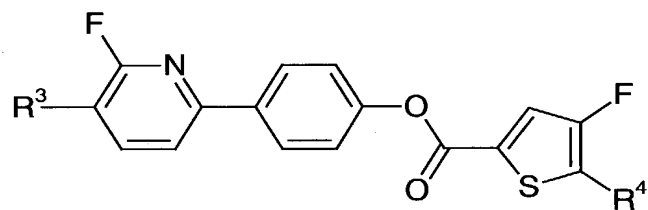
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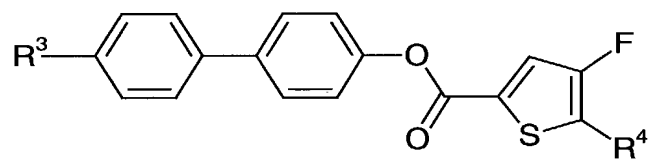
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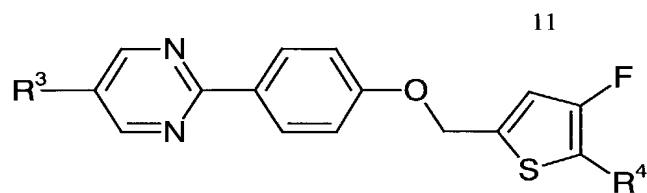
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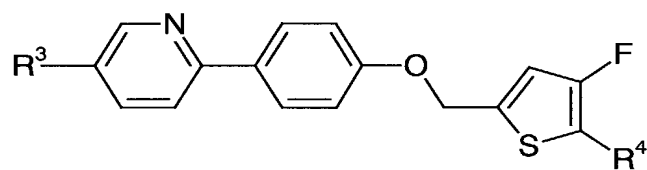
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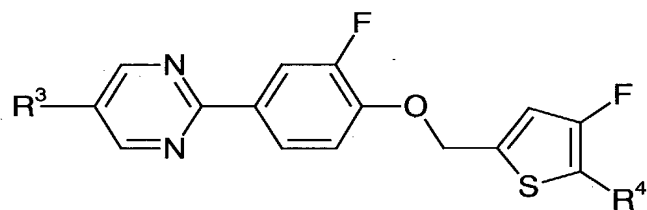
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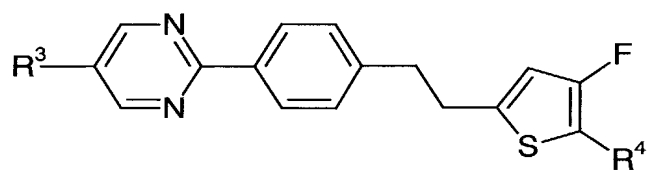
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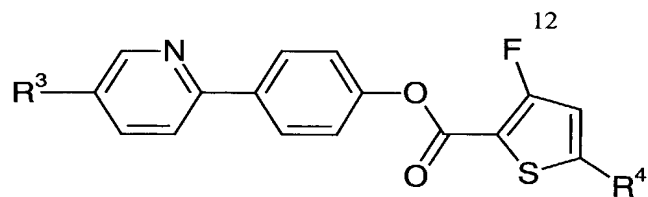
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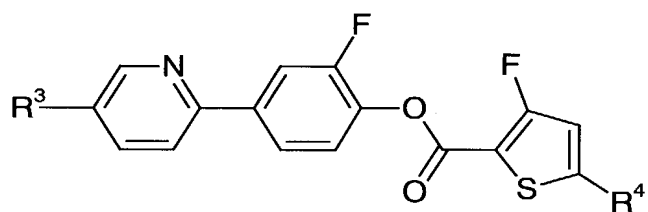
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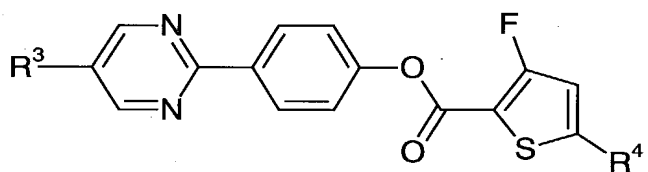
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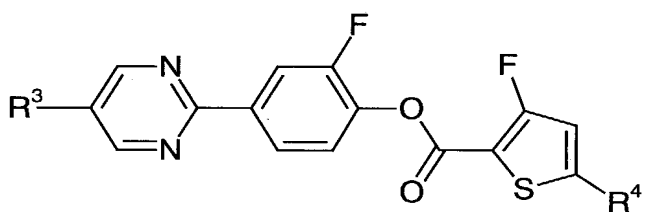
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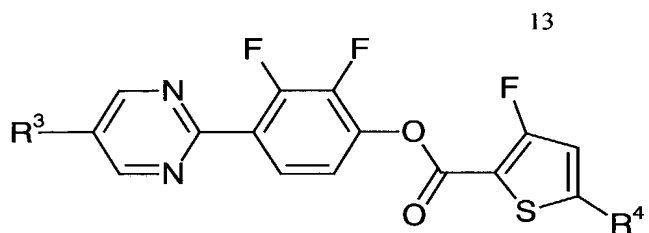
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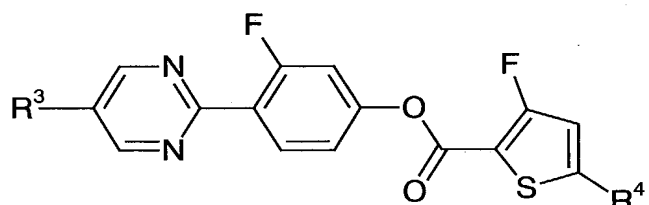
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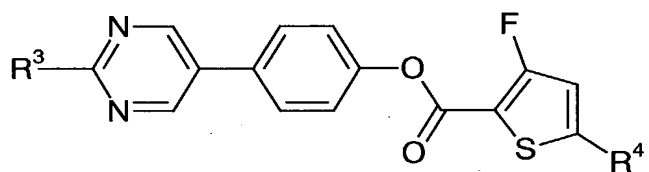
(I-20)



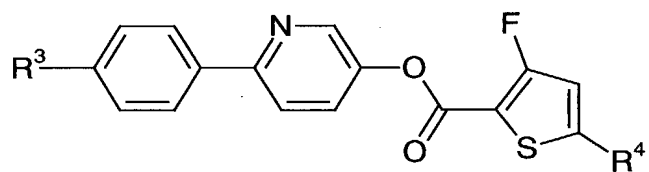
(I-21)



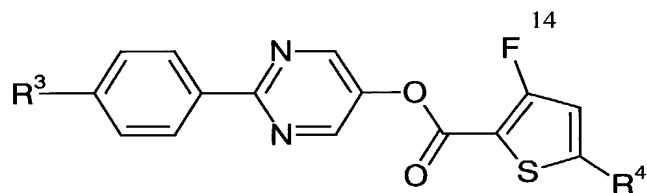
(I-23)



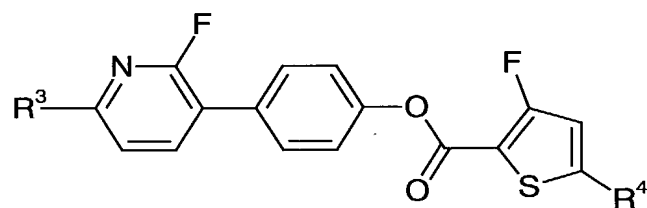
(I-24)



(I-25)

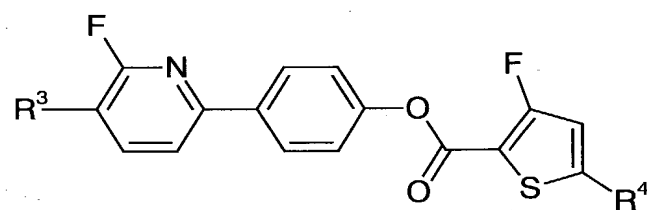


(I-26)



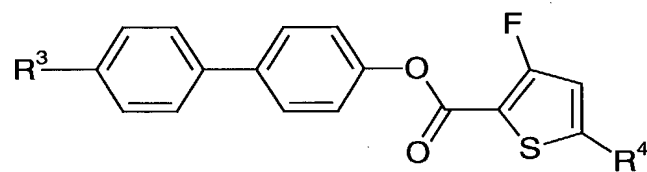
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(I-27)



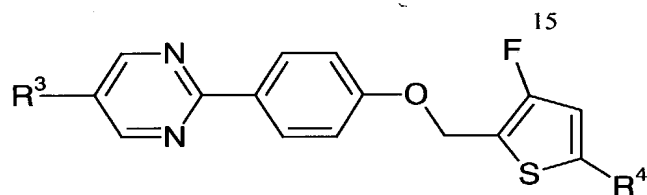
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(I-28)

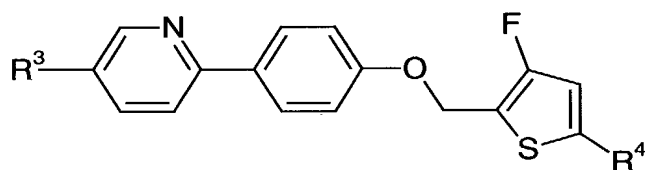


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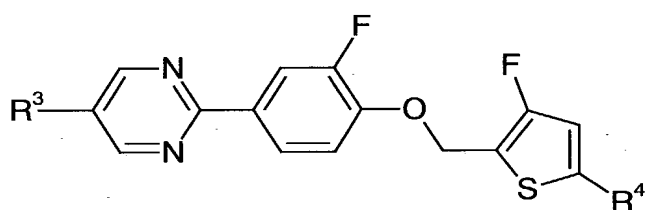
(I-29)



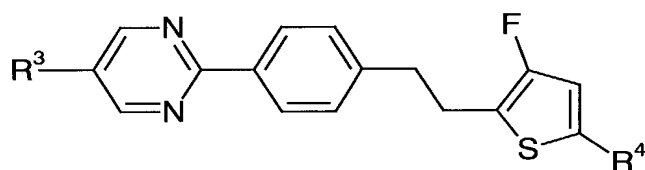
(I-30)



(I-31)



(I-32)



(I-33)

in which:

R^3 is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal

16

CH₂ group may, in addition, be replaced by -O- or, undirected, by -OC(=O)- and one or more H atoms may be replaced by F;

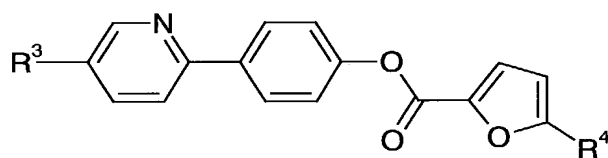
R⁴ is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-33), in which **R³** and **R⁴** are each, independently of one another, a straight-chain alkyl radical having 2 to 16 carbon atoms.

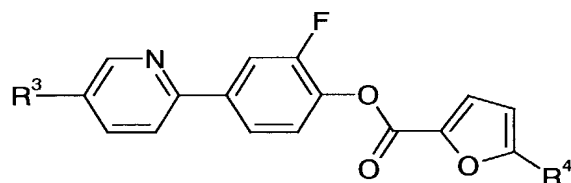
Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-33), in which **R³** is a straight-chain alkoxy radical having 2 to 12 carbon atoms and **R⁴** is hydrogen or a straight-chain alkyl radical having 2 to 12 carbon atoms.

Furan derivatives

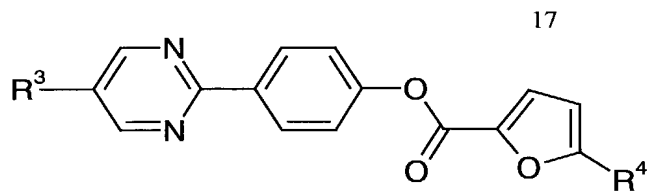
Preferred furan derivatives (ii) are the following compounds of the formulae (I-1) to (I-16)



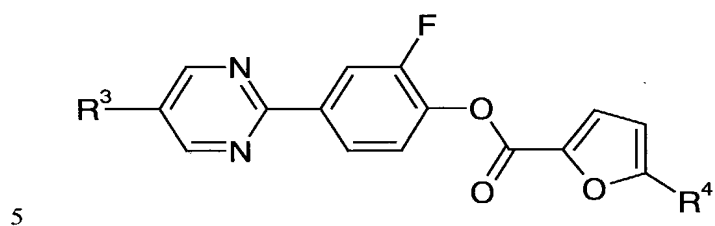
(I-1)



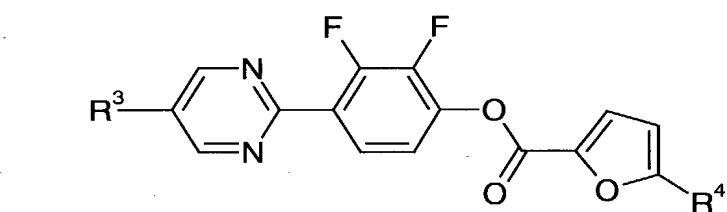
(I-2)



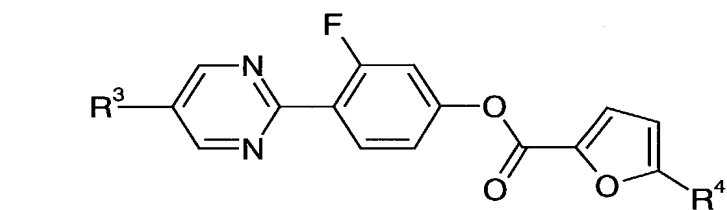
(I-3)



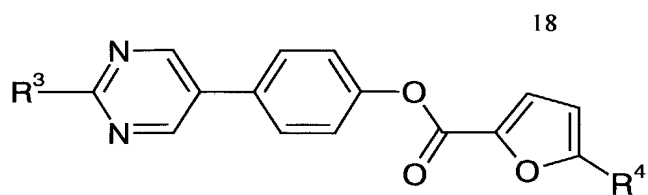
(I-4)



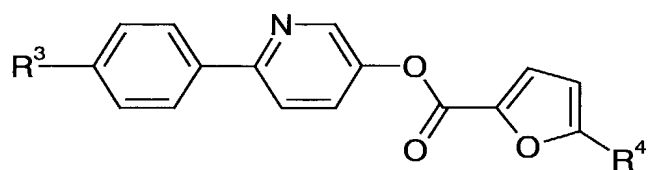
(I-5)



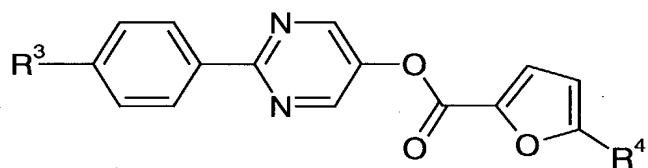
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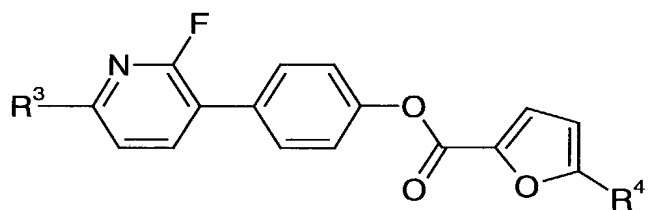
(I-7)



(I-8)

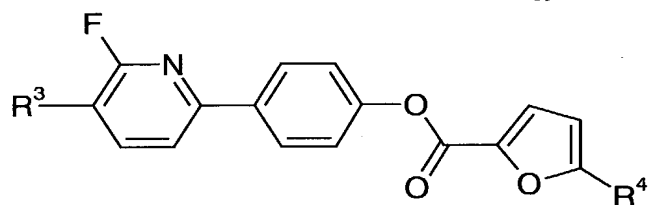


(I-9)

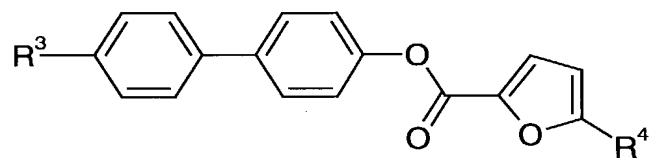


(I-10)

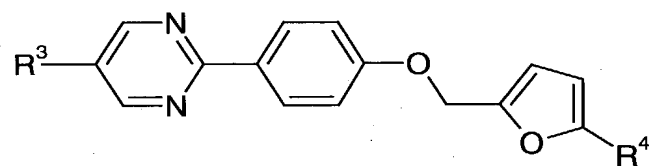
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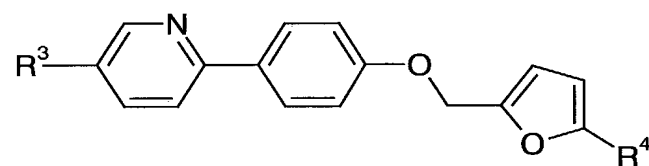
(I-11)



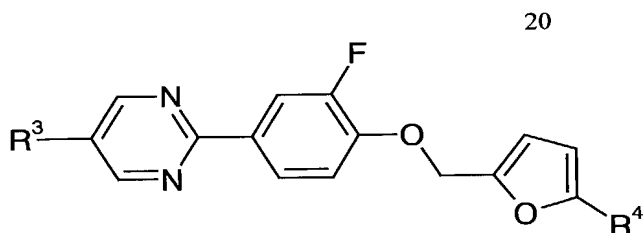
(I-12)



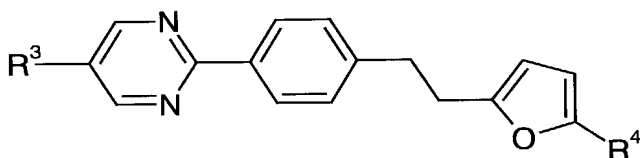
(I-13)



(I-14)



(I-15)



(I-16)

in which:

- 10 **R³** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or undirected -OC(=O)- and one or more H atoms may be replaced by F;
- 15 **R⁴** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

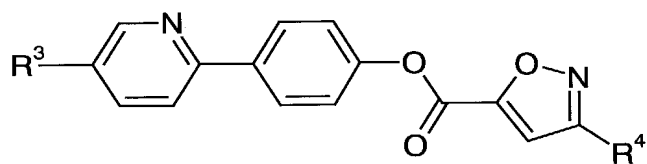
Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-16), in which **R³** and **R⁴** are each, independently of one another, a straight-chain alkyl radical having 2 to 16 carbon atoms.

Particular preference is likewise given to compounds of the formulae (I), in particular (I-1) to (I-16), in which **R³** is a straight-chain alkoxy radical having 2 to 12 carbon atoms and **R⁴** is hydrogen or a straight-chain alkyl radical having 2 to 12 carbon atoms.

Isoxazole derivatives

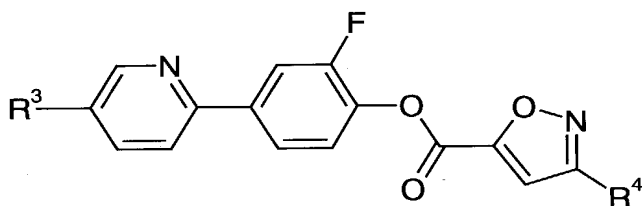
Preferred isoxazole derivatives (iii) are the following compounds of the formulae (I-1) to (I-15)

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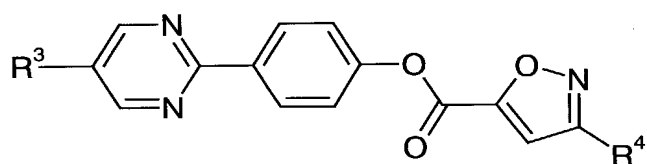
(I-1)

10



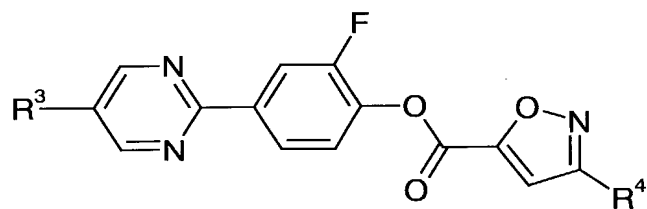
(I-2)

15



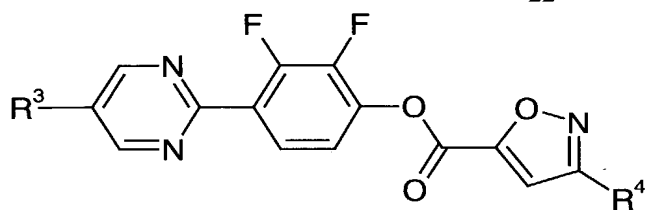
(I-3)

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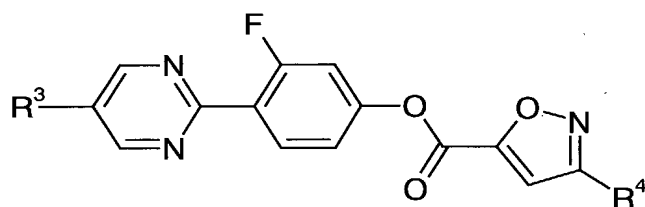
(I-4)

22



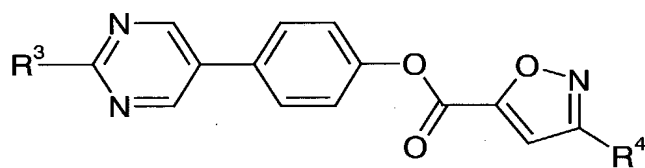
(I-5)

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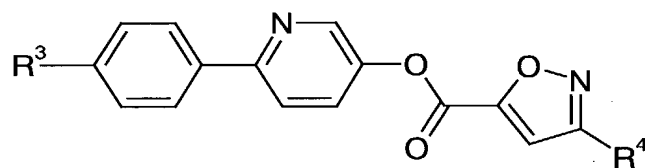


(I-6)

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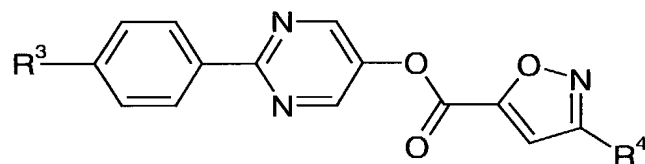


(I-7)



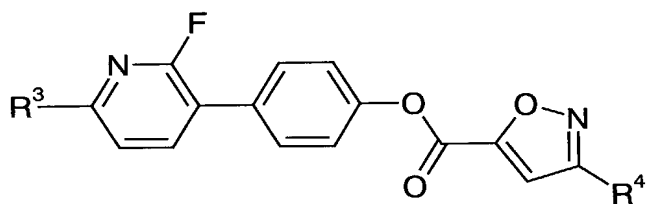
(I-8)

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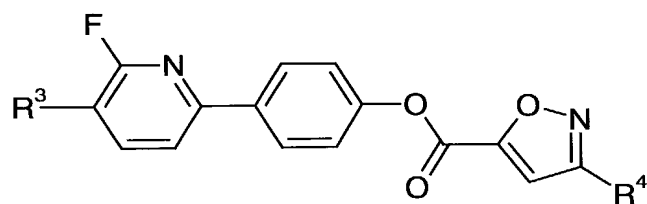
(I-9)

23



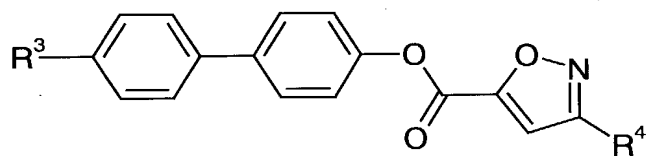
(I-10)

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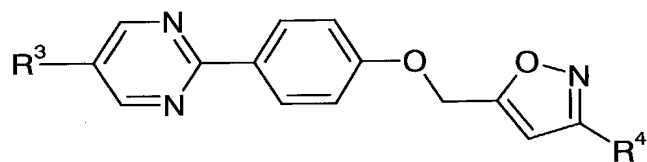
(I-11)

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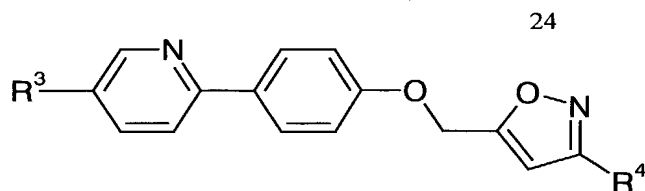


(I-12)

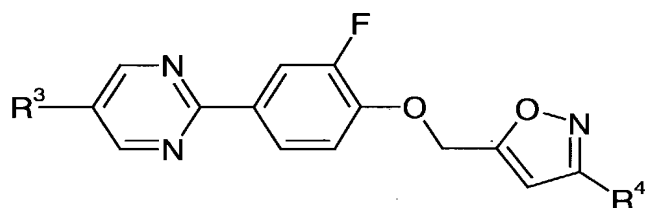
15



(I-13)



(I-14)



(I-15)

in which:

- 10 **R³** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or undirected -OC(=O)- and one or more H atoms may be replaced by F;
- 15 **R⁴** is hydrogen or a straight-chain or branched alkyl or alkyloxy radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

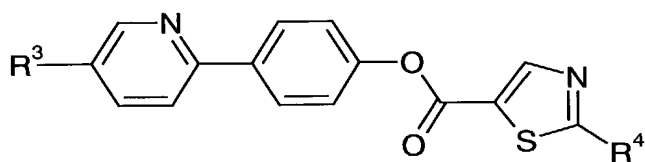
Particular preference is given to compounds of the formula (I), in particular (I-1) to (I-16), in which **R³** is a straight-chain alkyl radical having 2 to 16 carbon atoms and **R⁴** is a straight-chain alkyl or alkyloxy radical having 1 to 16 carbon atoms.

Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-16), in which **R³** is a straight-chain alkoxy radical having 2 to 12 carbon atoms and **R⁴** is a straight-chain alkyl or alkyloxy radical having 1 to 12 carbon atoms.

Thiazole derivatives

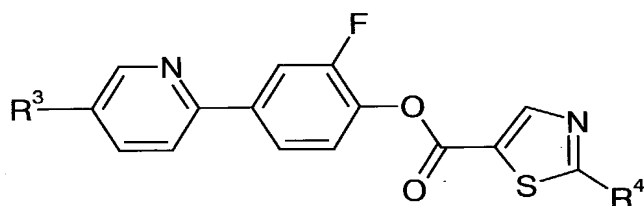
Preferred thiazole derivatives (iv) are the following compounds of the formulae (I-1) to (I-15)

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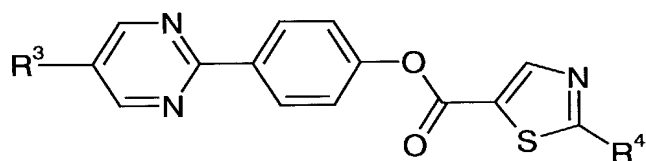
(I-1)

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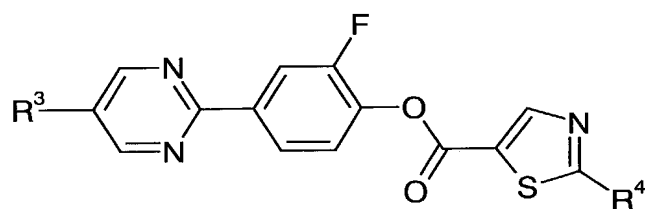
(I-2)

15



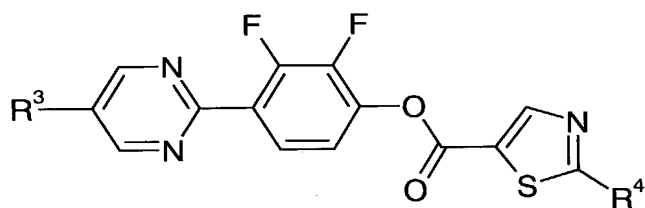
(I-3)

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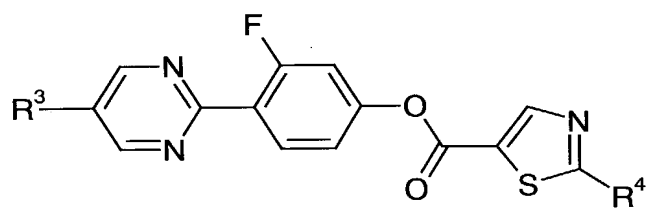
(I-4)

26



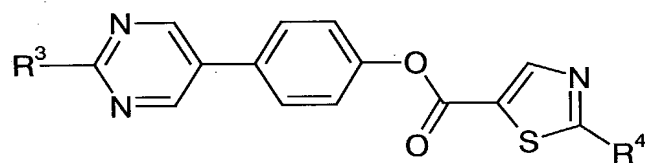
(I-5)

5



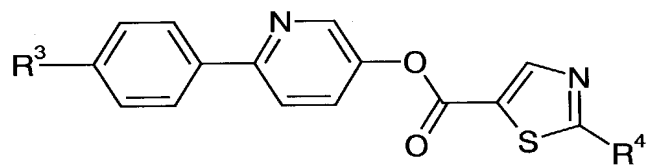
(I-6)

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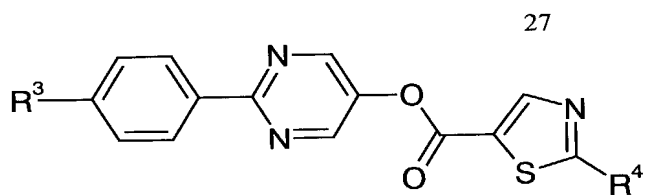


(I-7)

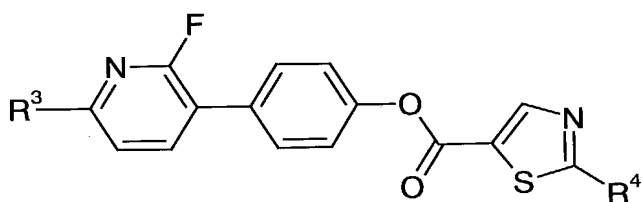
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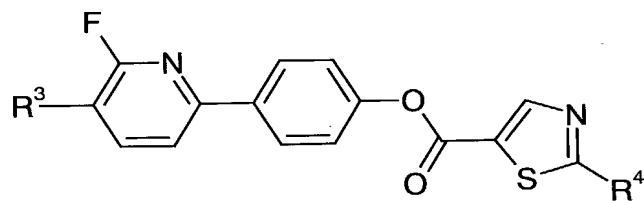
(I-8)



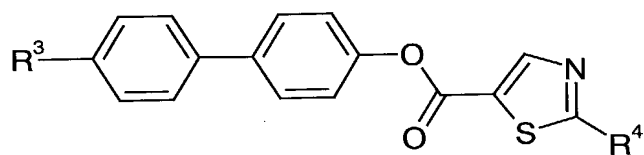
(I-9)



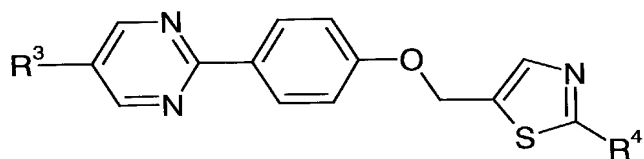
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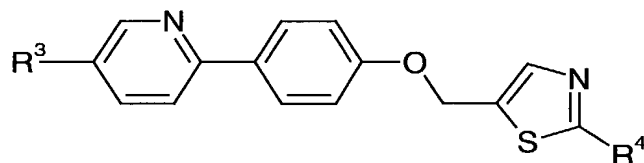
(I-11)



(I-12)

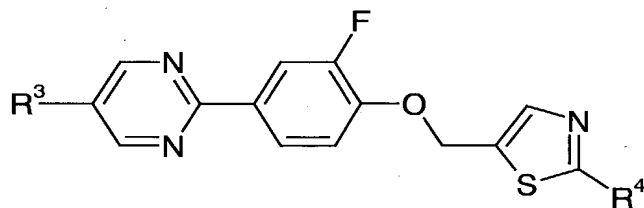


(I-13)



(I-14)

5



(I-15)

10 in which:

R³ is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or undirected -OC(=O)- and one or more H atoms may be replaced by F;

15

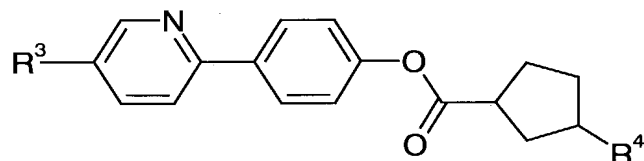
R⁴ is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-15), in which **R³** is a straight-chain alkyl radical having 2 to 16 carbon atoms and **R⁴** is a straight-chain alkyl radical having 1 to 16 carbon atoms.

Particular preference is likewise given to compounds of the formulae (I), in particular (I-1) to (I-15), in which **R³** is a straight-chain alkoxy radical having 2 to 12 carbon atoms and **R⁴** is a straight-chain alkyl radical having 1 to 12 carbon atoms.

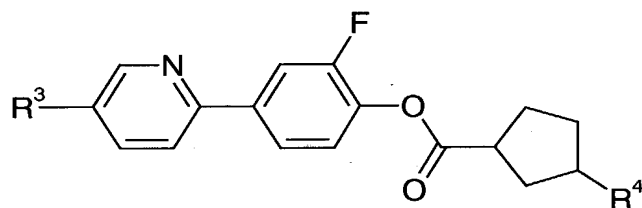
Cyclopentane derivatives

Preferred cyclopentane derivatives (v) are the following compounds of the
5 formulae (I-1) to (I-16)



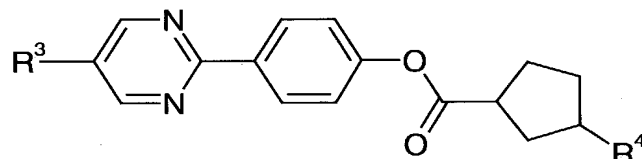
(I-1)

10



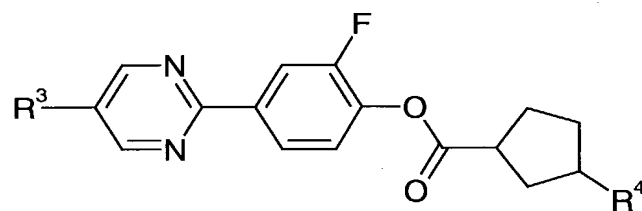
(I-2)

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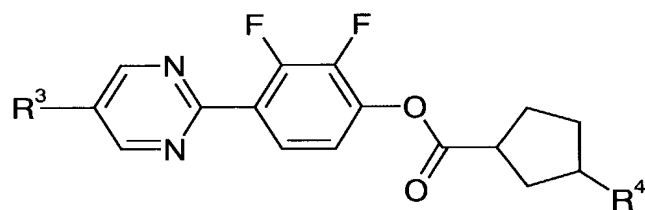
(I-3)

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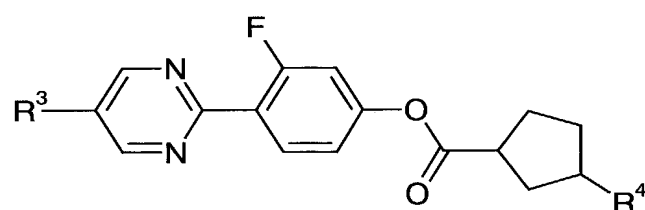
(I-4)

30



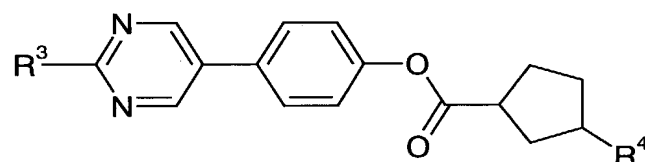
(I-5)

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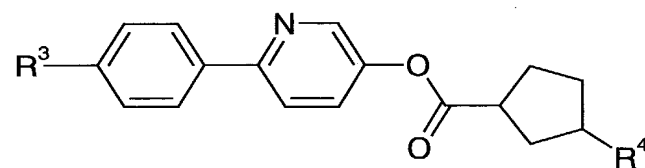
(I-6)

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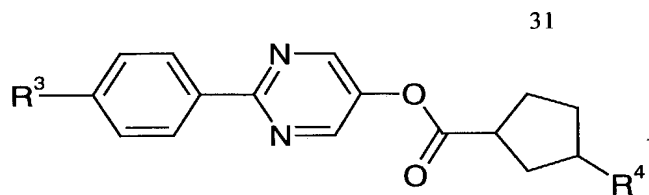


(I-7)

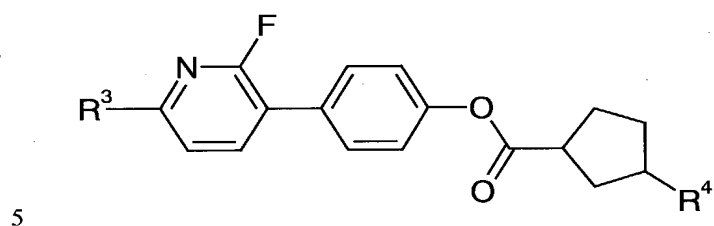
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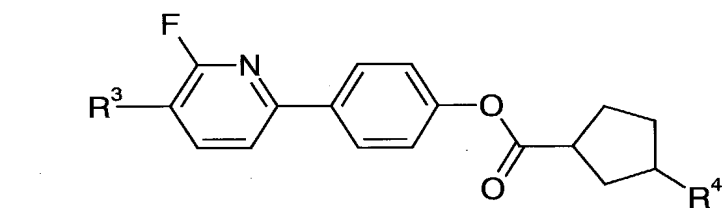
(I-8)



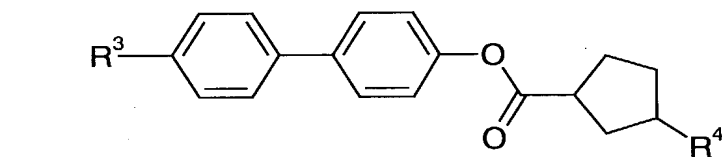
(I-9)



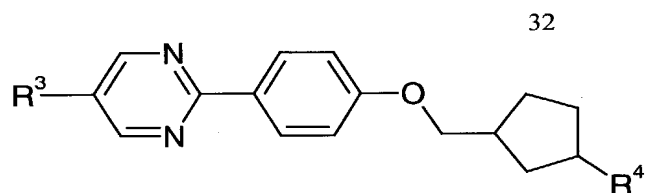
(I-10)



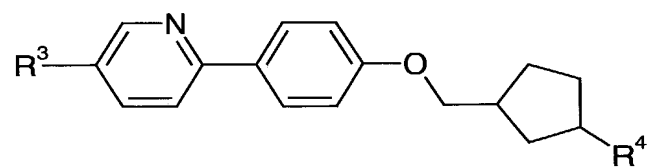
(I-11)



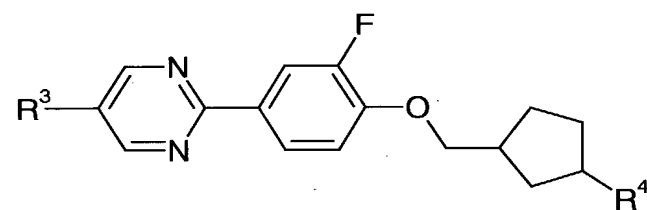
(I-12)



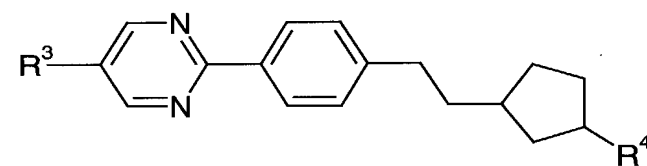
(I-13)



(I-14)



(I-15)



(I-16)

in which:

R³ is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal
20 CH₂ group may be replaced by -O- or undirected -OC(=O)- and one or more H atoms may be replaced by F;

R^4 is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

- 5 Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-16), in which R^3 and R^4 are each, independently of one another, a straight-chain alkyl radical having 2 to 16 carbon atoms.

10 Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-16), in which R^3 is a straight-chain alkoxy radical having 2 to 12 carbon atoms and R^4 is hydrogen or a straight-chain alkyl radical having 2 to 12 carbon atoms.

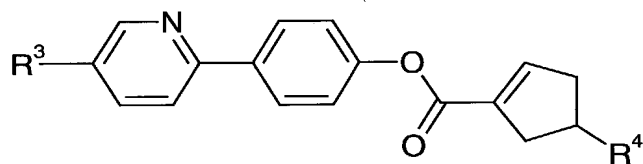
Cyclopentene derivatives

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T is preferably

1-cyclopentene-1,3-diyl, 1-cyclopentene-1,4-diyl or 3-cyclopentene-1,3-diyl.

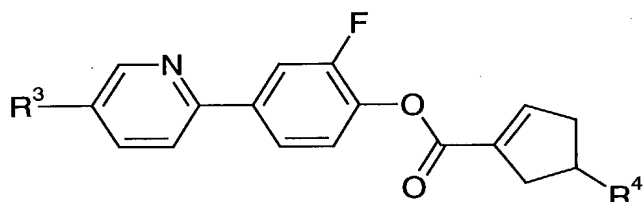
20 Preferred cyclopentene derivatives (vi) are the following compounds of the formulae (I-1) to (I-45)



(I-1)

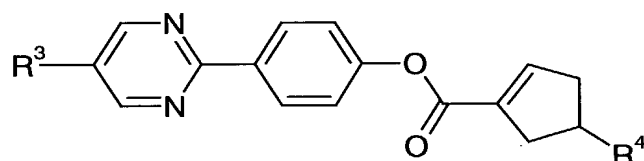
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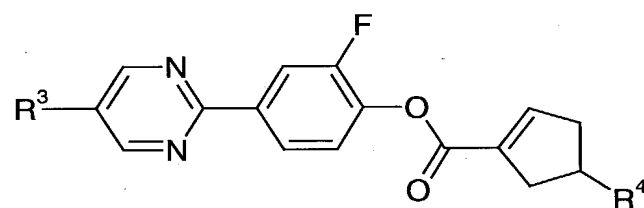
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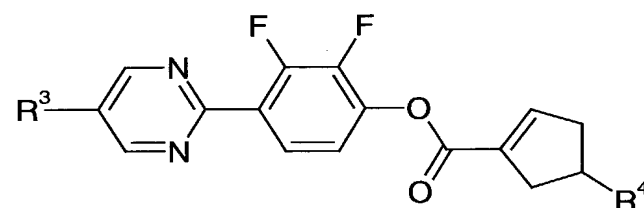
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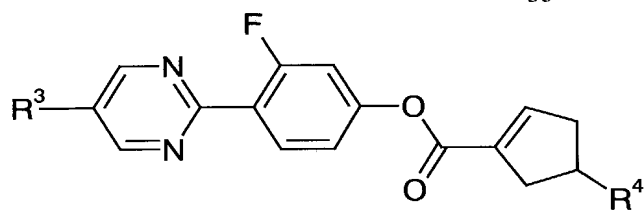
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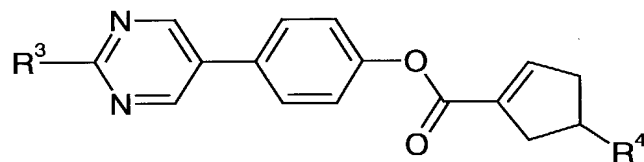


(I-5)

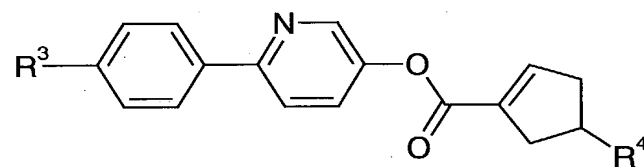
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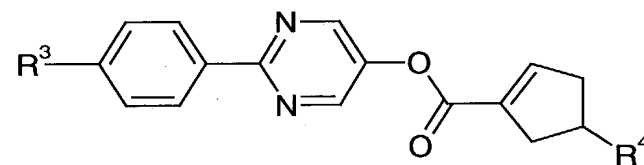
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(I-7)

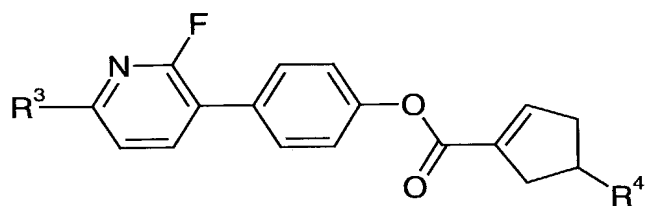


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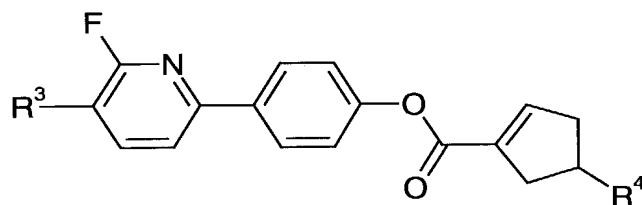


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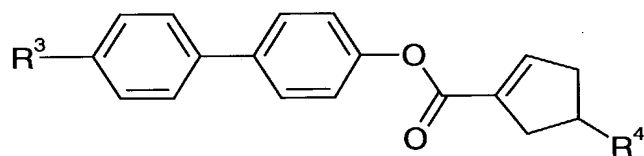
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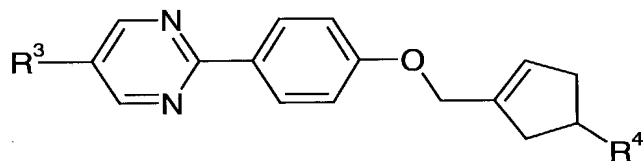
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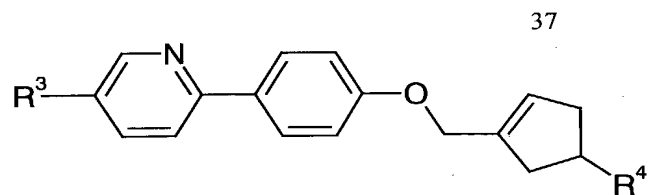
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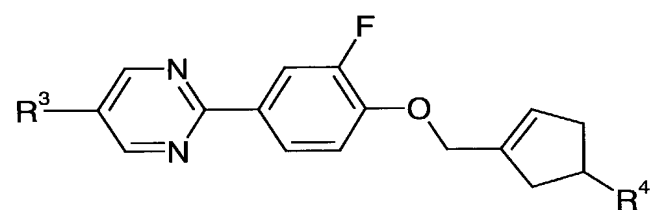
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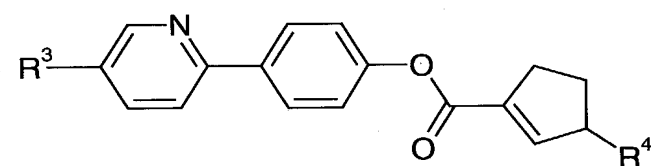
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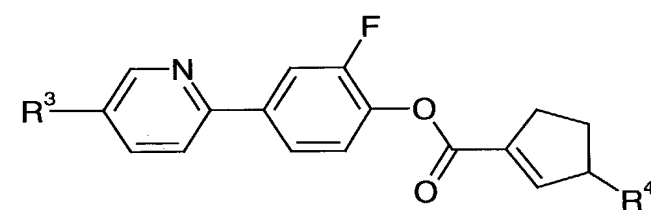
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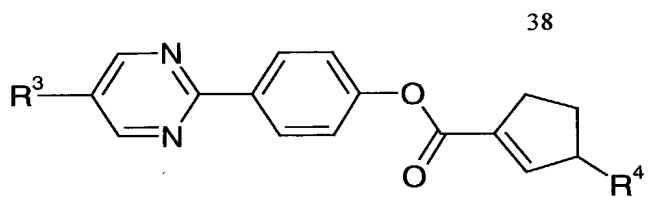
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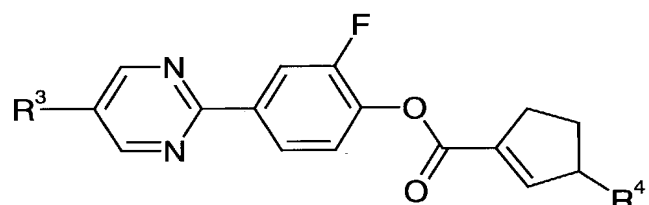
(I-16)



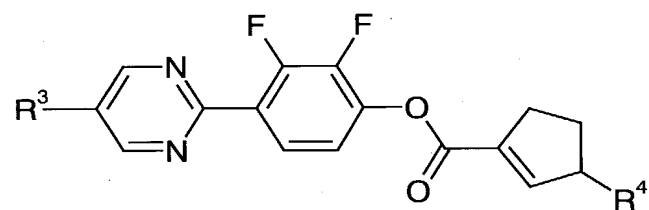
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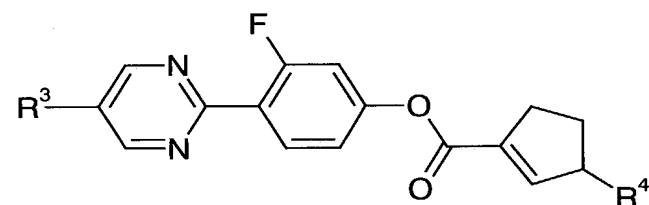
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(I-19)

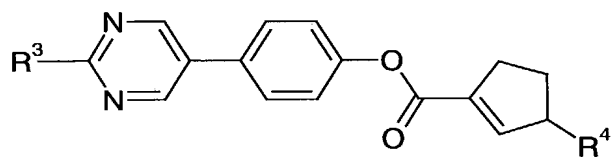


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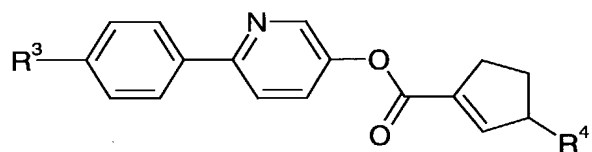
(I-21)

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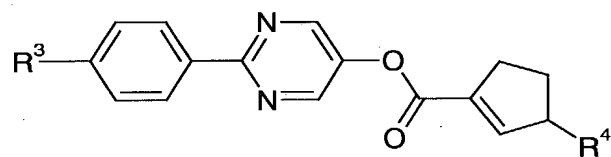
(I-22)

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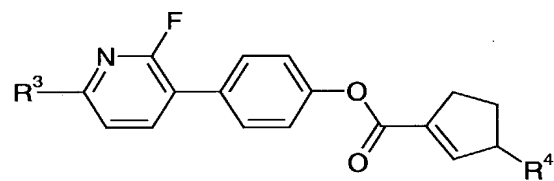
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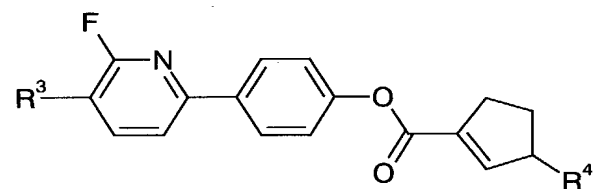


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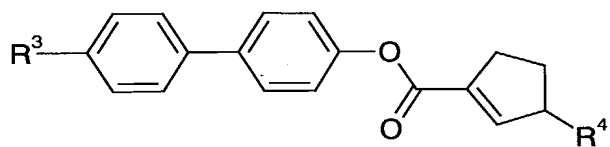


(I-25)

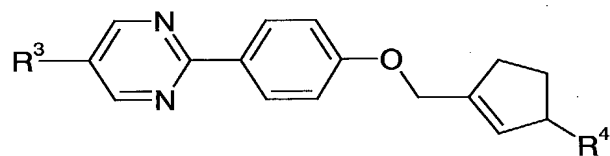


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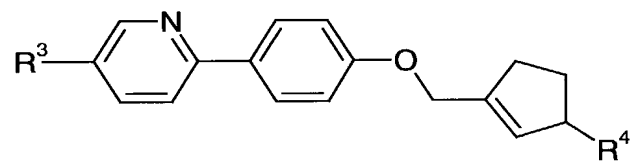
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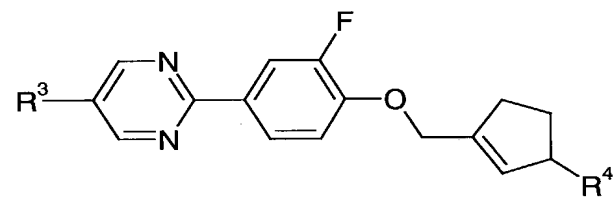
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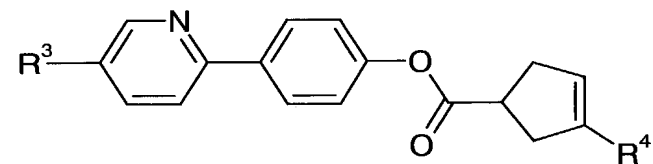
(I-28)



(I-29)

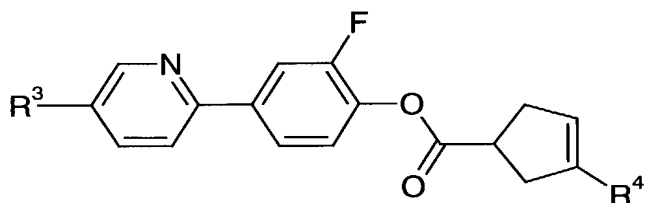


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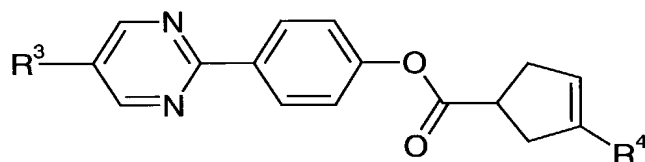


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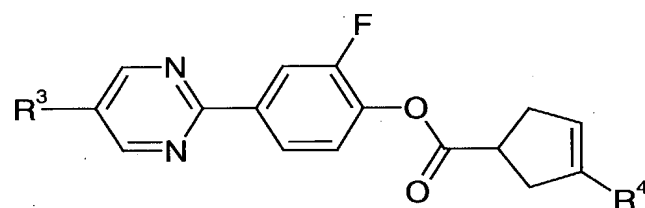
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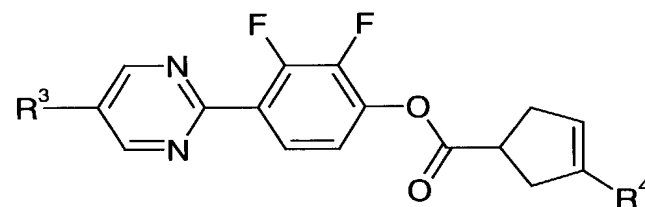
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(I-33)

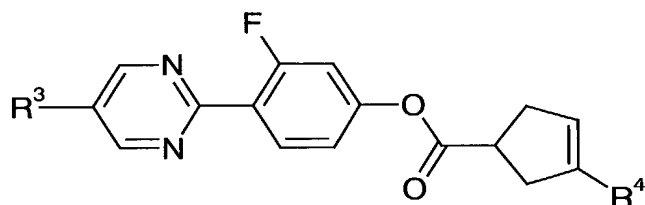


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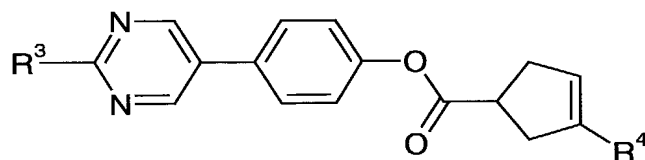


(I-35)

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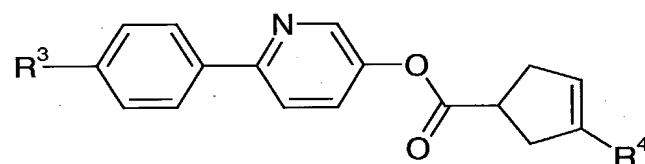


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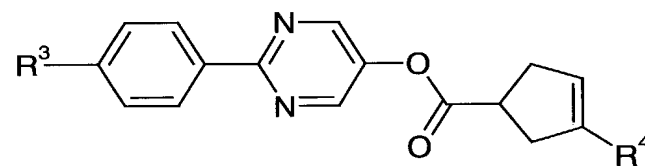
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(I-37)

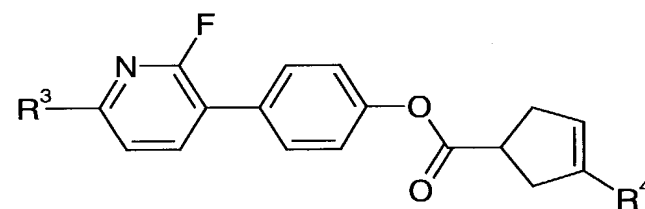


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(I-38)



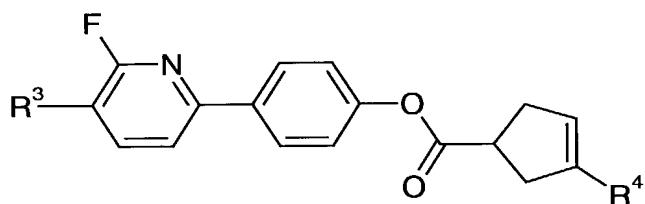
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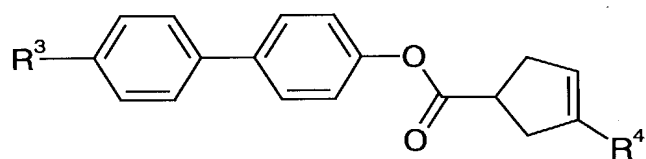
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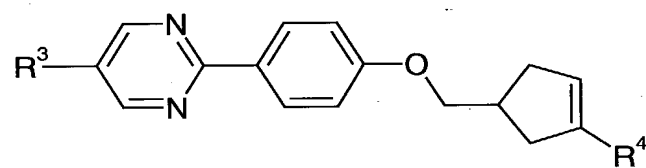
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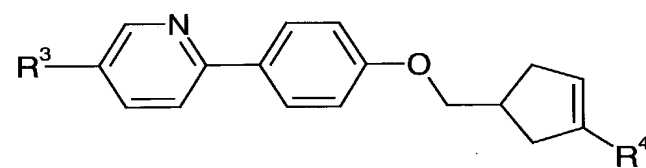
(I-42)

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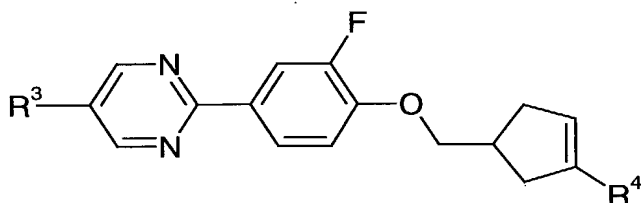
(I-43)

15



(I-44)

44



(I-45)

5 in which:

R^3 is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal CH_2 group may, in addition, be replaced by $-O-$ or, undirected, by $-OC(=O)-$ and one or more H atoms may be replaced by F;

10

R^4 is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-45), in which R^3 and R^4 are each, independently of one another, a straight-chain alkyl radical having 1 to 16 carbon atoms.

Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-45), in which R^3 is a straight-chain alkoxy radical having 2 to 12 carbon atoms and R^4 is hydrogen or a straight-chain alkyl radical having 1 to 12 carbon atoms.

Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-45), in which R^3 is a branched alkyl or alkyloxy radical having 2 to 12 carbon atoms and R^4 is hydrogen or a straight-chain alkyl radical having 1 to 12 carbon atoms.

Of the compounds of the formula (I) which are to be used as optically active components (dopants) in liquid-crystal mixtures, preference is given to those in

which the alkyl group contains the asymmetric carbon atoms in the form of at least one of the following groups:

- a) $-C^*H(CH_3)C_mH_{2m+1}$, where m has a value of from 2 to 8
- b) $-OC^*H(CH_3)C_mH_{2m+1}$, where m has a value of from 2 to 8
- 5 c) $-OC^*H(CH_3)CO_2C_mH_{2m+1}$, where m has a value of from 1 to 10
- d) $-OC(=O)C^*H(CH_3)OC_mH_{2m+1}$, where m has a value of from 1 to 10
- e) $-OC(=O)C^*H(F)C_mH_{2m+1}$, where m has a value of from 1 to 10
- f) $-OCH_2C^*H(F)C_mH_{2m+1}$, where m has a value of from 1 to 10
- g) $-OCH_2C^*H(F)C^*H(F)C_mH_{2m+1}$, where m has a value of from 1 to
- 10 10
- h) oxirane-2,3-diyl

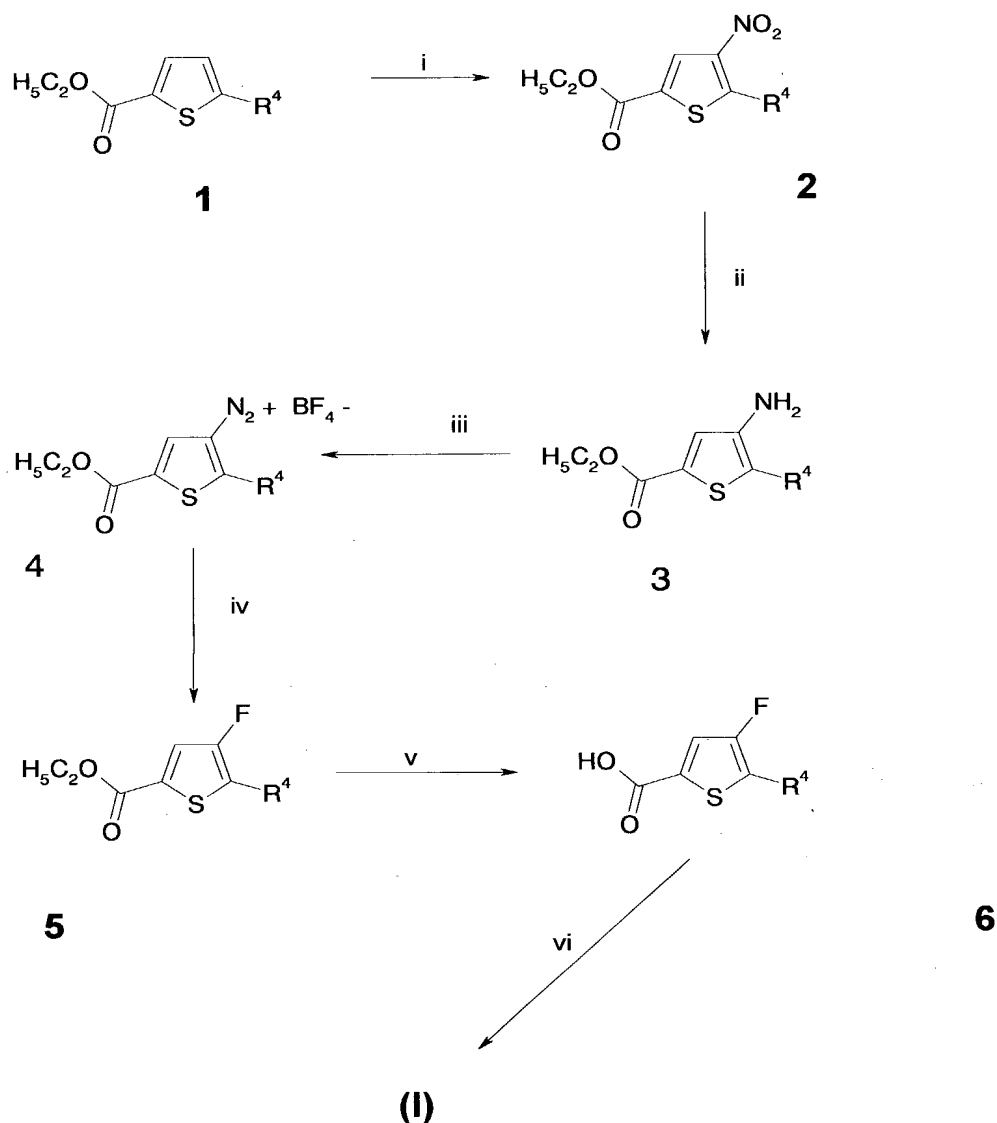
in which C* denotes the asymmetric carbon atom.

The compounds according to the invention are prepared by methods known per se
15 from the literature, as described in standard works on organic synthesis, for example Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart.

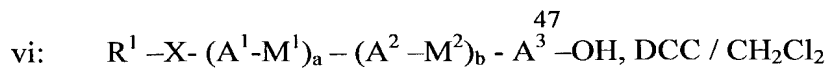
However, it may prove necessary to vary or modify the literature methods for the
20 requirements of mesogenic units, since, for example, functional derivatives having long ($> C_6$) alkyl chains tend to be less reactive than, for example, the methyl or ethyl analogues.

Particular reference is made in this connection to the following synthesis schemes
25 for thiophene derivatives (i), in which the synthesis of the thiophene derivatives of the invention is illustrated in more detail by way of example.

Scheme 1



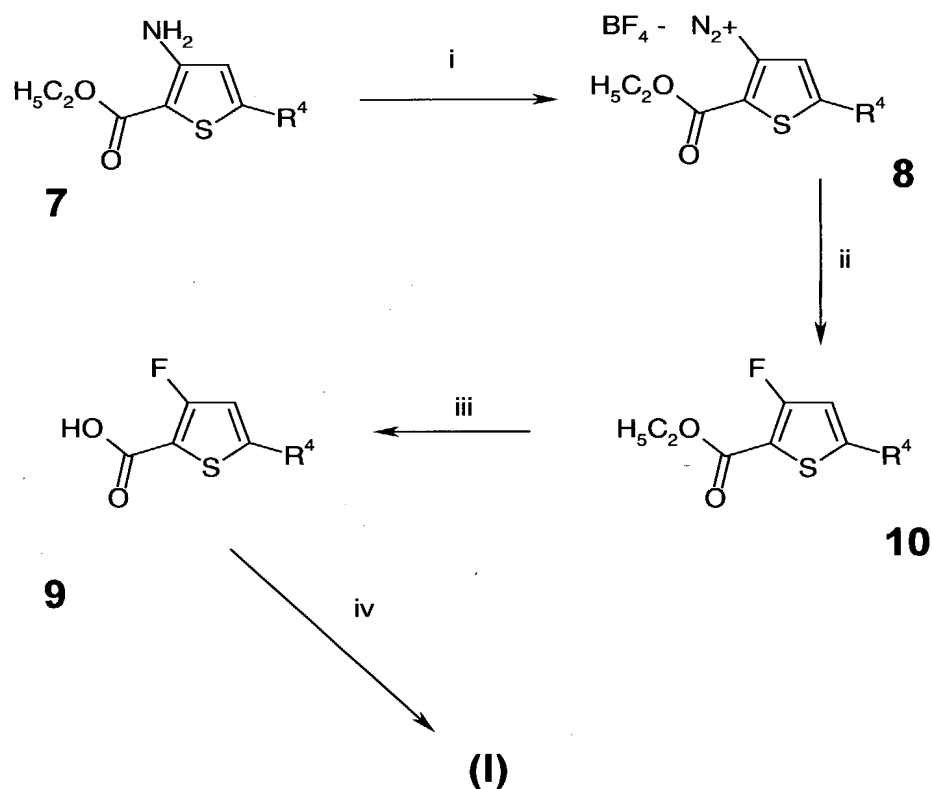
- 5 i: HNO₃, H₂SO₄ as described by Campaigne, J.Am.Chem.Soc. 73, 3812 (1951).
- ii: Sn, HCl as described by Dewar, J.Am.Chem.Soc. 84, 3782 (1962)
- iii: 1. NaNO₂ 2. HBF₄ as described by Corral, Heterocycles 23, 1431 (1985)
- iv: Thermolysis as described by Corral, Heterocycles 23, 1431 (1985)
- 10 v: 1. NaOH, EtOH 2. H⁺ as described by Corral, Heterocycles 23, 1431 (1985)



The 5-alkylthiophene-2-carboxylic esters **1** required for the synthesis in accordance with Scheme 1 are prepared as described in EP-B 0 500 072.

5

Scheme 2

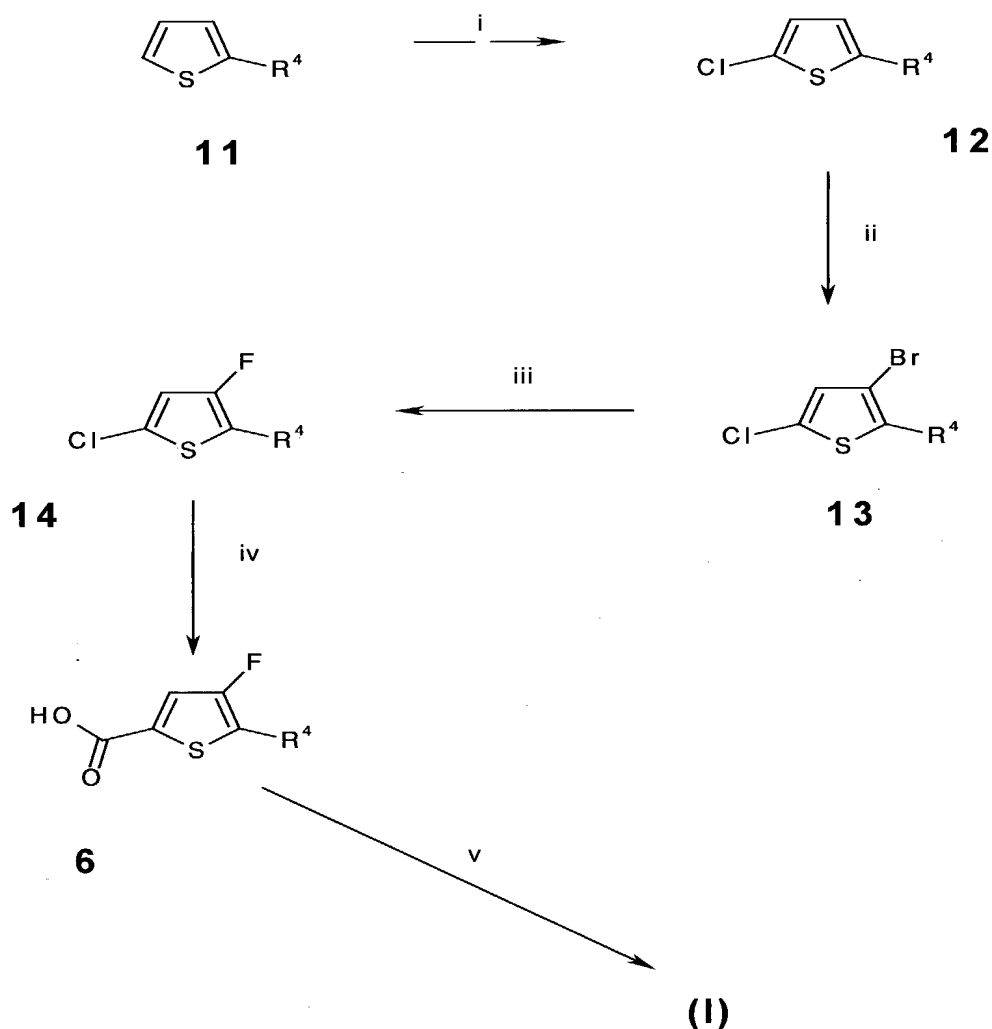


- 10 i: 1. $NaNO_2$ 2. HBF_4 as described by Corral, Heterocycles 23, 1431 (1985)
 ii: Thermolysis as described by Corral, Heterocycles 23, 1431 (1985)
 iii: 1. $NaOH$, $EtOH$ 2. H^+ as described by Corral, Heterocycles 23, 1431 (1985)
 iv: $R^1-X-(A^1-M^1)_a-(A^2-M^2)_b-A^3-OH$, DCC / CH_2Cl_2

15

The 5-alkyl-3-amino-thiophene-2-carboxylic esters **7** required for the synthesis in accordance with Scheme 2 are prepared as described by Huddleston, Synth. Commun. 9, 731 (1979) or in JP-A 05117263 or JP-A 06025221.

5 Scheme 3

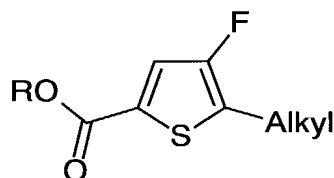


- i: N-chlorosuccinimide, HOAc, benzene as described by Lucas, Tetrahedron Lett. 40, 1775 (1999)
- ii: Br₂, CHCl₃ as described by Lucas, Tetrahedron Lett. 40, 1775 (1999)
- iii: 1. BuLi 2. F-TEDA-BF₄; step 1 as described by Lucas, Tetrahedron Lett. 40, 1775 (1999)

iv: 1. BuLi 2. CO₂ as described by Lucas, Tetrahedron Lett. 40, 1775 (1999)

v: $R^1-X-(A^1-M^1)_a-(A^2-M^2)_b-A^3-OH$, DCC / CH₂Cl₂

The invention furthermore provides the intermediate 5-alkyl-4-fluoro-thiophene-2-
5 carboxylic acids of the formula (II)

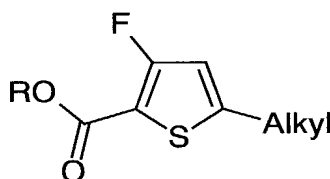


(II)

10 in which alkyl is a straight-chain or branched alkyl radical of 2 to 16 carbon atoms
and R is hydrogen, alkali metal, alkaline earth metal (1/2), a straight-chain or
branched alkyl radical of 1 to 16 atoms with the exception of methyl and tert-
butyl, and

5-alkyl-3-fluoro-thiophene-2-carboxylic acids of the formula (III)

15



(III)

in which alkyl is a straight-chain or branched alkyl radical of 2 to 16 carbon atoms
20 and R is hydrogen, alkali metal, alkaline earth metal (1/2), a straight-chain or
branched alkyl radical of 1 to 16 atoms and corresponding acid halides, in
particular acid chlorides, thereof.

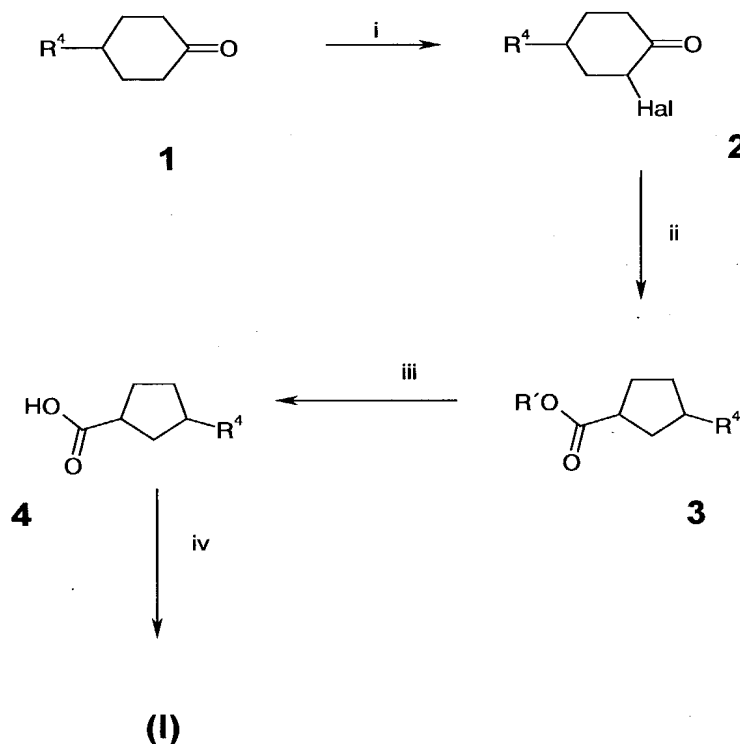
Some of them correspond to the abovementioned compounds of the formulae 5, 6,
25 9 and 10. They can be used for preparing liquid crystals, agrochemicals and
pharmaceuticals.

The 2-alkylthiophenes **11** required for the synthesis in accordance with Scheme 3 can be obtained as described in EP-B 0 500 072.

- 5 In this context, in particular for cyclopentane derivatives, reference is made to the synthesis schemes below in which the synthesis of the cyclopentane derivatives according to the invention is illustrated in more detail by way of example.

Scheme 1

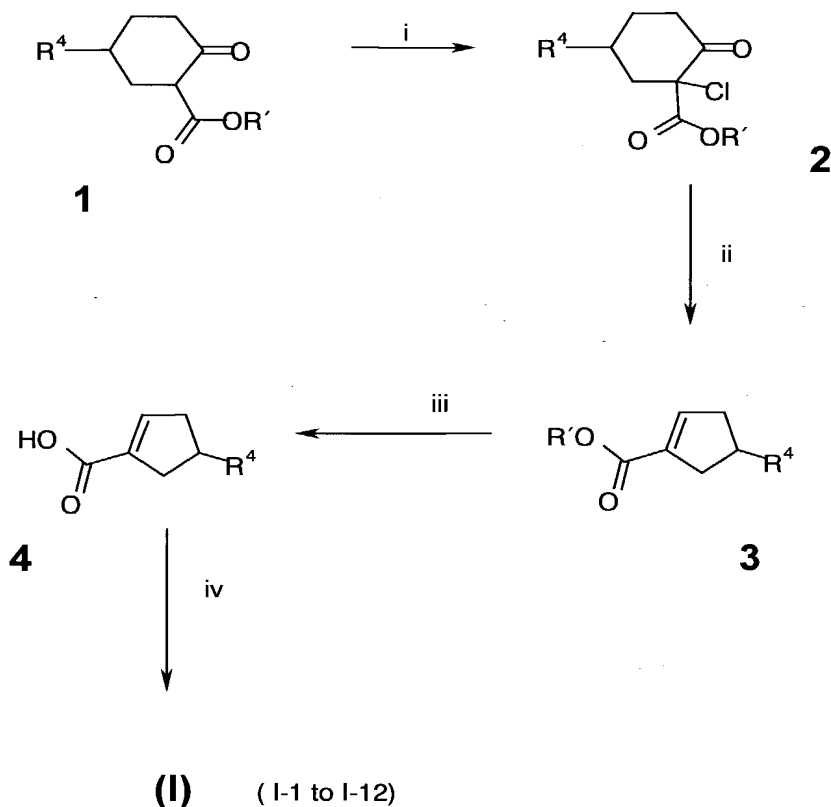
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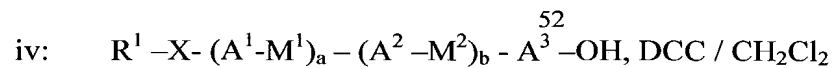
- i: N-bromosuccinimide, CCl_4 as described by Corey, *J. Am. Chem. Soc.* 75, 2301 (1953).
- 15 ii: NaOCH_3 , tert-butyl methyl ether as described in *Organic Syntheses, Coll. Vol. IV*, 594
- iii: 1. $\text{NaOH} / \text{H}_2\text{O}$ 2. HCl
- iv: $\text{R}^1 - \text{X} - (\text{A}^1 - \text{M}^1)_a - (\text{A}^2 - \text{M}^2)_b - \text{A}^3 - \text{OH}$, $\text{DCC} / \text{CH}_2\text{Cl}_2$

5 In this context, in particular for cyclopentene derivatives, reference is made to the synthesis schemes below in which the synthesis of the cyclopentene derivatives according to the invention is illustrated in more detail by way of example.

10

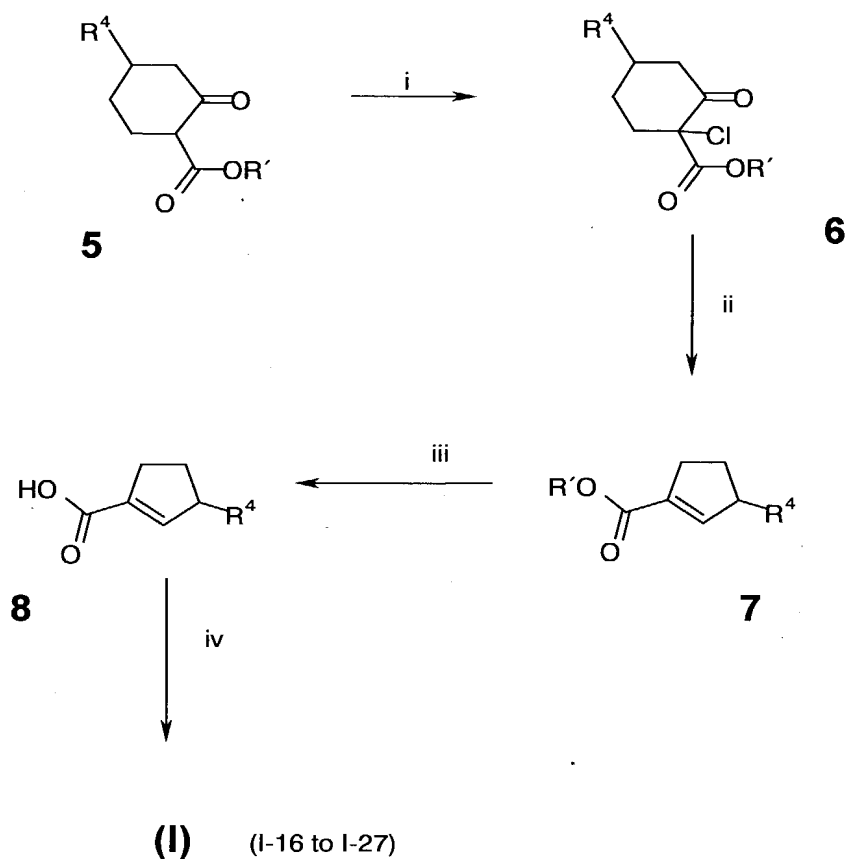


- i: t-BuOCl, CH₃OH as described by Takeda, *Bull.Chem.Soc.Jpn.* 50(7), 1831 (1977).
- 15 ii: Na₂CO₃, xylene, 160°C as described by Takeda, *Bull.Chem.Soc.Jpn.* 50(7), 1831 (1977).
- iii: 1. NaOH/ H₂O 2. HCl



Scheme 2

5



i: $t\text{-BuOCl}$, CH_3OH as described by Takeda, *Bull.Chem.Soc.Jpn.* 50(7), 1831 (1977).

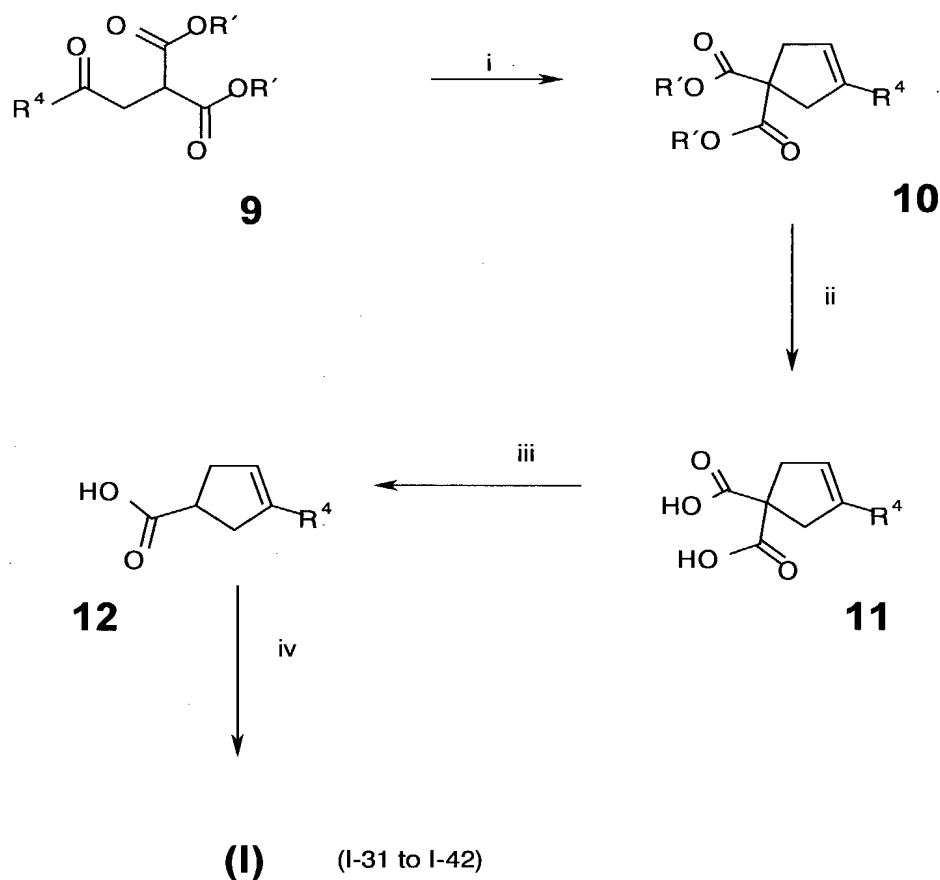
10 ii: Na_2CO_3 , xylene, $160^\circ C$ as described by Takeda, *Bull.Chem.Soc.Jpn.* 50(7), 1831 (1977).

iii: 1. $NaOH/H_2O$ 2. HCl

iv: $R^1-X-(A^1-M^1)_a-(A^2-M^2)_b-A^3-OH$, DCC / CH_2Cl_2

The starting materials **1** and **5** required for the syntheses in accordance with schemes 1 and 2, respectively, can be prepared as described by Eisenbraun et al., J.Org.Chem. 32, 3010 (1967).

5

Scheme 3

- 10 i: Vinyltriphenylphosphonium bromide (Schweizer's Reagent), NaH, Et₂O as described by Schweizer, *J.Org.Chem.* 30, 2082 (1965).
- ii: 1.KOH 2.HCl as described by Schweizer, *J.Org.Chem.* 30, 2082 (1965).
- iii: Thermolysis as described by Schweizer, *J.Org.Chem.* 30, 2082 (1965).
- iv: R¹-X- (A¹-M¹)_a - (A²-M²)_b - A³-OH, DCC / CH₂Cl₂

15

The starting materials **9** required for the synthesis in accordance with Scheme 3 can be prepared as described by Hurd et al., J.Am.Chem.Soc. 70, 1650 (1948).

As far as the linking of functional derivatives of the furans, isoxazoles, thiazoles, cyclopentanes, cyclopentenenes and fluorinated thiophenes with other liquid-crystal-specific units is concerned, express reference is made to DE-A 197 48 432, which gives a list of methods customary to the person skilled in the art.

The invention furthermore provides the use of compounds of the formula (I) in liquid-crystal mixtures, preferably smectic and nematic liquid-crystal mixtures, particularly preferably chiral smectic (ferroelectric) liquid-crystal mixtures. Particular preference is given to the use in ferroelectric liquid-crystal mixtures operated in inverse mode or in displays comprising active matrix elements. Very particular preference is given to the use in mixtures for active matrix LCDs in which the chiral smectic liquid-crystal layer forms a monostable monodomain.

The invention furthermore provides liquid-crystal mixtures, preferably smectic and nematic liquid-crystal mixtures, particularly preferably ferroelectric (chiral smectic) liquid-crystal mixtures, which comprise one or more compounds of the formula (I).

The liquid-crystal mixtures according to the invention generally comprise from 2 to 35 components, preferably from 2 to 25 components, particularly preferably from 2 to 20 components.

They generally comprise from 0.01 to 80% by weight, preferably from 0.1 to 60% by weight, particularly preferably from 0.1 to 30% by weight, based on the entire mixture, of one or more, preferably from 1 to 10, particularly preferably from 1 to 5, very particularly preferably from 1 to 3, compounds of the formula (I) according to the invention.

Further components of liquid-crystal mixtures which comprise compounds of the formula (I) according to the invention are preferably selected from known compounds having smectic and/or nematic and/or cholesteric phases. Further mixture components which are suitable in this context are listed, in particular, in international patent application PCT/EP96/03154 and in DE-A 197 48 432, which are incorporated herein by reference.

The mixtures according to the invention can in turn be used in electro-optical or fully optical elements, for example display elements, switching elements, light modulators, elements for image processing and/or signal processing, or generally in the area of nonlinear optics.

The invention therefore furthermore provides a switching and/or display device containing a liquid-crystal mixture, preferably a smectic liquid-crystal mixture, which comprises one or more compounds of the formula (I).

Particular preference is given to ferroelectric switching and/or display devices comprising active matrix elements (cf. e.g. DE-A 198 22 830).

The present application cites various documents, for example in order to illustrate the technical background to the invention. All these documents are incorporated herein by reference.

The examples which follow illustrate the invention.

Thiophene derivatives

Example 1

4-(5-Undecyl-pyrimidin-2-yl)phenyl 4-fluoro-5-propyl-thiophene-2-carboxylate

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 2.0 g of 4-fluoro-5-propyl-thiophene-2-carboxylic acid (prepared in accordance with Scheme 1 by nitrating methyl

5-propyl-thiophene-2-carboxylate in $\text{HNO}_3/\text{H}_2\text{SO}_4$ to form methyl 4-nitro-5-propyl-thiophene-2-carboxylate, followed by reduction of the latter by means of Sn / HCl to give the corresponding amino compound, conversion of the latter into the diazonium tetrafluoroborate, thermolysis and, finally, hydrolysis) and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the target compound as colorless crystals.

10

The compounds (I-1) to (I-12) can be obtained in a similar manner, and the compounds (I-17) to (I-29) can be obtained in a similar manner using the 5-alkyl-3-fluoro-thiophene-2-carboxylic acids prepared in accordance with Scheme 2.

15

Example 2

(4-Fluoro-5-propyl-thiophen-2-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-pyrimidin-2-yl)phenol and 4-fluoro-5-propyl-thiophen-2-yl-methanol (prepared by LiAlH_4 reduction of methyl 4-fluoro-5-propyl-thiophene-2-carboxylate). After 24 h at room temperature the mixture is evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

25

The compounds (I-13) to (I-15) and (I-30) to (I-32) can be obtained in a similar manner.

The compounds of the formulae (I-16) and (I-33) can be obtained via the sequence 4-(or 3-)fluoro-5-alkyl-thiophen-2-yl-methanol -- 2-bromomethyl-4-(or 3-)fluoro-5-alkyl-thiophene -- 2-bromomethyl-5-alkyl-4-(or 3-)fluoro-thiophen-2-yl-

30

triphenylphosphonium salt -- Wittig reaction with 4-(5-R³-pyrimidin-2-yl)benzaldehyde -- hydrogenation.

Furan derivatives

5

Example 1

4-(5-Undecyl-pyrimidin-2-yl)phenyl 5-ethyl-furan-2-carboxylate

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.4 g of 5-ethyl-2-furancarboxylic acid (prepared as described by Perry et al., Appl.Organomet.Chem. 10, 389-392
10 (1996) from furan-2-carboxylic acid; m.p. 90°C) and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the target compound as colorless crystals
15 having the phase sequence X 80 (N62) I.

The following compound is prepared in a similar manner

Example 2

20 **2-Fluoro-4-(5-undecyl-pyridin-2-yl)phenyl 5-ethyl-furan-2-carboxylate**
which has a melting point of 76°C.

The compounds (I-1) to (I-12) can be prepared similarly to Example 1.

Example 3

(5-Ethyl-furan-2-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol and 5-ethyl-furan-2-yl-methanol (prepared by
30 LiAlH₄ reduction of methyl 5-ethyl-furan-2-carboxylate, which in turn can be obtained by esterification of 5-ethyl-furan-2-carboxylic acid from Example 1). The mixture is stirred for 24 h at room temperature and then evaporated to dryness

under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

The compounds (I-13) to (I-15) can be obtained in a similar manner.

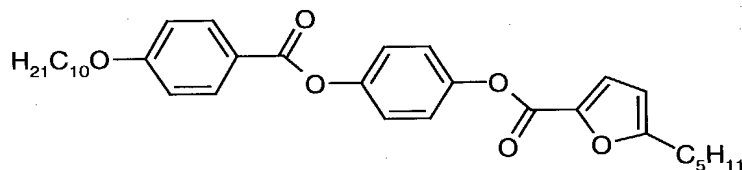
5

The compounds of the formula (I-16) can be obtained via the sequence 5-ethyl-furan-2-yl-methanol -- 2-bromomethyl-5-ethyl-furan -- 2-bromomethyl-5-ethyl-furan-triphenylphosphonium salt -- Wittig reaction with 4-(5-R³-pyrimidin-2-yl)benzaldehyde -- hydrogenation.

10

The following compounds were obtained in a similar manner:

Example 4



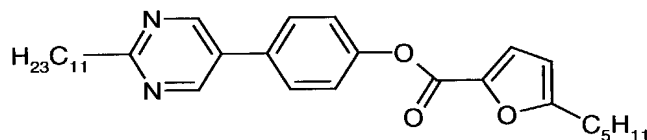
15

X 95 (N 92) I

4-(4-Decyloxy-benzoyloxy)phenyl 5-pentylfuran-2-carboxylate

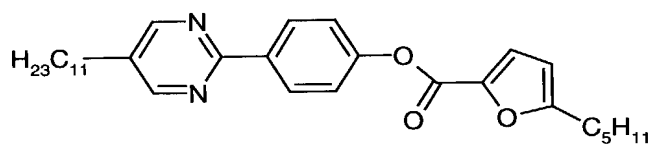
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Example 5

X 87 (S_A 86) I

25

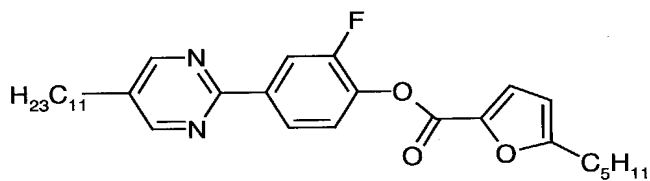
4-(2-Undecyl-pyrimidin-5-yl)phenyl 5-pentylfuran-2-carboxylate

Example 6

X 79 I

5

4-(5-Undecyl-pyrimidin-2-yl)phenyl 5-pentylfuran-2-carboxylate

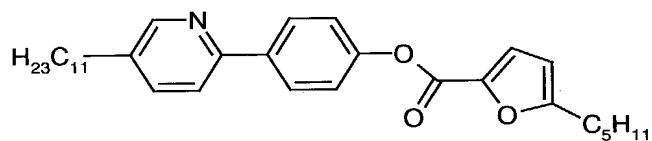
Example 7

10

X 83 I

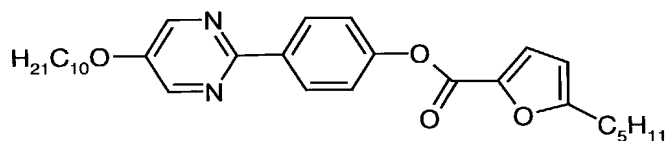
2-Fluoro-4-(5-undecyl-pyrimidin-2-yl)phenyl 5-pentylfuran-2-carboxylate

15

Example 8X 88 (S_A 68 N 69) I

20

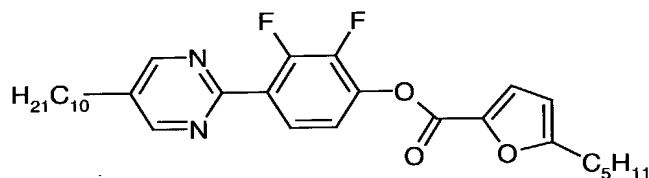
4-(5-Undecyl-pyridin-2-yl)phenyl 5-pentylfuran-2-carboxylate

Example 9

X 90 (N 90) I

5

4-(5-Decyloxy-pyrimidin-2-yl)phenyl 5-pentylfuran-2-carboxylate

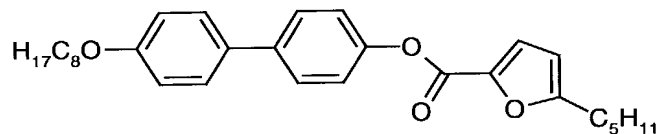
Example 10

10

X 67 I

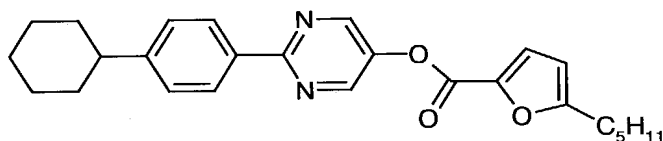
2,3-Difluoro-4-(5-decyl-pyrimidin-2-yl)phenyl 5-pentylfuran-2-carboxylate

15

Example 11X 78 S_C 94 S_A 96 I

20

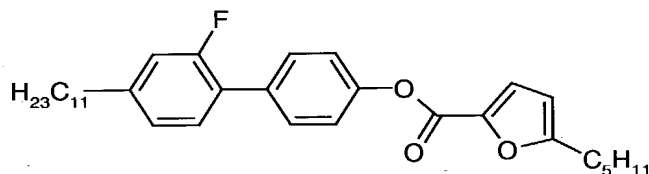
4-(4-Octyloxyphenyl)phenyl 5-pentylfuran-2-carboxylate

Example 12

X 142 I

5

2-(4-Cyclohexylphenyl)pyrimidin-5-yl 5-pentylfuran-2-carboxylate

Example 13

10

X 74 I

4-(2-Fluoro-4-undecyl-phenyl)phenyl 5-pentylfuran-2-carboxylate

15 Isoxazole derivatives**Example 1****4-(5-Undecyl-pyrimidin-2-yl)phenyl 3-propyloxy-isoxazole-5-carboxylate**

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.7 g of 3-propyloxy-isoxazole-5-carboxylic acid (prepared as described by Xue et al., Bioorg.Med.Chem.Letters 8 (1998) 3499 by reacting methyl 3-hydroxy-isoxazole-5-carboxylate, which is commercially available, with 1-bromopropane at 60°C in dimethylformamide / potassium carbonate followed by hydrolysis with LiOH in tetrahydrofuran) and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and

recrystallization from acetonitrile affords the target compound as colorless crystals having the phase sequence X 91 S_A 109 N 126 I.

The compounds (I-1) to (I-12) in which R⁴ is an alkoxy radical can be prepared similarly to Example 1, and the compounds (I-1) to (I-12) in which R⁴ is an alkyl radical can likewise be prepared using 3-alkyl-isoxazole-5-carboxylic acids prepared as described by Dulin et al., Proc.Soc.exp.Biol.Med., 1966, 121, 777.

Example 2

(3-Propyloxy-isoxazol-5-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-pyrimidin-2-yl)phenol and 3-propyloxy-isoxazol-5-yl-methanol (prepared by LiAlH₄ reduction of methyl 3-propyloxy-isoxazole-5-carboxylate). The mixture is stirred for 24 h at room temperature and then evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

The compounds (I-13) to (I-15) can be prepared in a similar manner.

Thiazole derivatives

Example 1

[4-(5-Undecyl-pyrimidin-2-yl)phenyl] 2-propyl-thiazole-5-carboxylate

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.7 g of 2-propyl-thiazole-5-carboxylic acid (prepared as described by Clemence et al., Eur.J.Med.Chem.-Chimica Therapeutica 1976-11, no.6, p.567-570) and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the target compound as colorless crystals.

The compounds (I-1) to (I-12) can be prepared in a similar manner to Example 1.

Example 2

5 (2-Propyl-thiazol-5-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-pyrimidin-2-yl)phenol and 2-propylthiazol-5-yl-methanol (prepared by LiAlH_4 reduction of methyl 2-propylthiazole-5-carboxylate). The mixture is stirred for 24
10 h at room temperature and then evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

The compounds (I-13) to (I-15) can be obtained in a similar manner.

15

Cyclopentane derivatives

Example 1

4-(5-Undecyl-pyrimidin-2-yl)phenyl 3-ethyl-cyclopentanecarboxylate

20 4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.5 g of 3-ethyl-cyclopentane-carboxylic acid and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the
25 target compound as colorless crystals.

The compounds (I-1) to (I-12) can be obtained in a similar manner.

Example 2

30 4-(5-Undecyl-pyrimidin-2-yl)phenyl (3-ethyl-cyclopentan-1-yl)methyl ether

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-

pyrimidin-2-yl)phenol and 3-ethyl-cyclopentan-1-yl-methanol (prepared by LiAlH₄ reduction of methyl 3-ethyl-cyclopentanecarboxylic acid). The mixture is stirred for 24 h at room temperature and then evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and
5 recrystallization affords the target compound.

The compounds (I-13) to (I-15) can be obtained in a similar manner.

The compounds of the formulae (I-16) and (I-33) can be obtained via the sequence

10 *3-alkyl-cyclopentan-1-yl-methanol*

1-bromomethyl-3-alkyl-cyclopentane

(1-bromomethyl-3-alkyl-cyclopentane)triphenylphosphonium salt

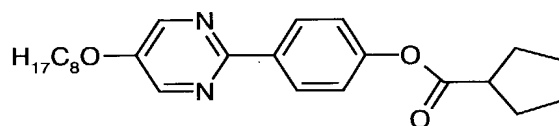
Wittig reaction with 4-(5-R³-pyrimidin-2-yl)benzaldehyde

hydrogenation

15

The following compounds were obtained in a similar manner:

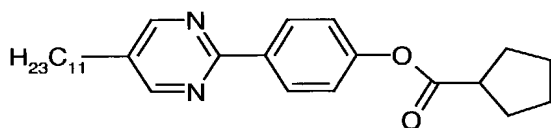
Example 3



20

X 95 I

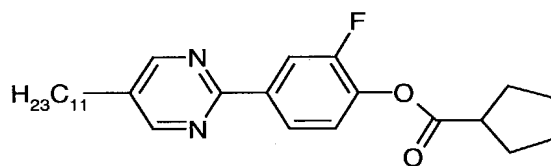
4-(5-Octyloxy-pyrimidin-2-yl)phenyl cyclopentanecarboxylate

Example 4

X 73 I

5

4-(5-Undecyl-pyrimidin-2-yl)phenyl cyclopentanecarboxylate

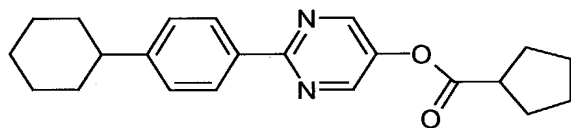
Example 5

X 66 I

10

2-Fluoro-4-(5-undecyl-pyrimidin-2-yl)phenyl cyclopentanecarboxylate

15

Example 6

X 164 I

20

2-(4-Cyclohexyl)phenyl-pyrimidin-5-yl cyclopentanecarboxylate

Cyclopentene derivatives**Example 1**

25

4-(5-Undecyl-pyrimidin-2-yl)phenyl 3-ethyl-1-cyclopentene-1-carboxylate

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.5 g of 3-ethyl-1-cyclopentene-1-carboxylic acid and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml

of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the target compound.

5

The compounds (I-1) to (I-12), (I-16) to (I-27) and (I-31) to (I-42) can be obtained in a similar manner.

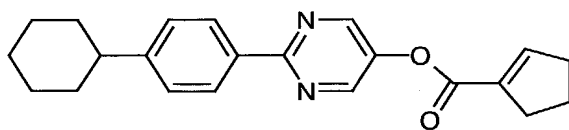
Example 2

10 (3-Ethyl-1-cyclopenten-1-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-pyrimidin-2-yl)phenol and 3-ethyl-1-cyclopenten-1-yl-methanol (prepared by LiAlH₄ reduction of methyl 3-ethyl-1-cyclopentene-1-carboxylate as described by
15 Takeda, Bull.Chem.Soc.Jpn. 50 (7),1831 (1977)). The mixture is stirred for 24 h at room temperature and then evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

20 The compounds (I-13) to (I-15), (I-28) to (I-30) and (I-43) to (I-45) can be obtained in a similar manner.

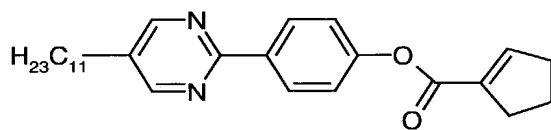
The following compounds were obtained in a similar manner:



5

2-(4-Cyclohexyl)phenyl-pyrimidin-5-yl cyclopent-1-ene-1-carboxylate

Example 4



10

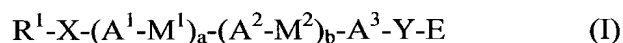
X 109 I

4-(5-Undecyl-pyrimidin-2-yl)phenyl cyclopent-1-ene-1-carboxylate

Patent claims

5

1. A five-membered ring compound of the formula (I),



10 where the symbols and indices have the following meanings:

E is a radical $T-Z-R^2$ containing a five-membered ring, where:

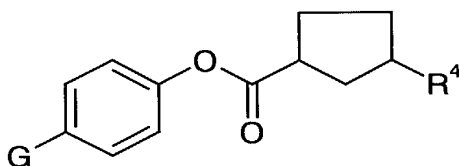
- (i) **T** is undirected and is
 15 4-fluorothiophene-2,5-diyl, 3-fluorothiophene-2,5-diyl,
 3-fluorothiophene-2,4-diyl or 5-fluorothiophene-2,4-diyl
Z is a single bond or -O-
R² is hydrogen or a straight-chain or branched alkyl radical (with or
 without asymmetric carbon atoms) having 1 to 20 carbon atoms,
 20 where one nonterminal CH₂ group may be replaced by -O- or
 -OC(=O)- or -C(=O)O- and/or one or more H atoms may be
 replaced by F, with the provisos that
 b) the -CH₂- group nearest to the thiophene cannot be replaced by
 -O- when Z is -O-
 25 b) R² can only be hydrogen when Z is a single bond,
- (ii) **T** is furan-2,5-diyl or furan-2,4-diyl
Z is a single bond or -O-
 30 **R²** is hydrogen or a straight-chain or branched alkyl radical (with or
 without asymmetric carbon atoms) having 1 to 20 carbon atoms,
 where one nonterminal CH₂ group nonadjacent to furan may be

replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F,

- (iii) **T** is undirected and is isoxazole-3,5-diyl
5 **Z** is a single bond or -O-
- R²** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or
10 -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that
a) the -CH₂- group nearest to the isoxazole cannot be replaced by -O- when Z is -O-
b) R² can only be hydrogen when Z is a single bond,
15
- (iv) **T** is undirected and is thiazole-2,5-diyl or thiazole-2,4-diyl
Z is a single bond
R² is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms,
20 where one nonterminal CH₂ group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F,
- (v) **T** is cyclopentane-1,3-diyl
25 **Z** is a single bond or -O-
R² is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH₂ group may be replaced by -O- or
-OC(=O)- or -C(=O)O- and/or one or more H atoms may be
30 replaced by F, with the provisos that
a) the -CH₂- group nearest to the cyclopentane cannot be replaced by -O- when Z is -O-

b) R^2 can only be hydrogen when Z is a single bond,

with the exception of compounds of the formula (II)



(II)

in which

R^4 is as defined for R^2

G is trans-4-propyl-cyclohexyl or trans-4-butyl-cyclohexyl or an alkyl group of 1 to 15 carbon atoms, in which, in addition, one or more nonadjacent CH_2 groups may be replaced by -O-, -CO-, -OCO-, -O-CO-O-, -CHhalogen-, -CHCN- and/or -CH=CH- or is F, CN,

(vi) **T** is cyclopentane-1,3-diyl, in which one - CH_2CH_2 - or - CH_2CH - group is replaced by a -CH=CH- or -CH=C- group respectively

Z is a single bond

R^2 is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH_2 group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the proviso that the - CH_2 - group nearest to the cyclopentene cannot be replaced and where

Y cannot be - CH_2-CH_2 -,

25

R^1 is hydrogen or a straight-chain or branched C_{1-20} -alkyl or C_{2-20} -alkenyl radical (with or without asymmetric carbon atoms), where

- a) one or two nonterminal CH₂ groups may be replaced, independently of one another, by -O- or -C(=O)-, with the proviso that two adjacent CH₂ groups cannot be replaced in the same way, and/or
- b) one CH₂ group may be replaced by -C≡C-, and/or
- 5 c) one CH₂ group may be replaced by -Si(CH₃)₂-, cyclopropane-1,2-diyl, cyclobutane-1,3-diyl, cyclopentane-1,4-diyl, bicyclo[1.1.1]pentane-1,3-diyl or cyclohexane-1,4-diyl, and/or
- d) one or more H atoms may be replaced by F and/or CN,
- 10 e) in the case of a branched alkyl radical containing asymmetric carbon atoms, the asymmetric carbon atoms have -CH₃, -OCH₃, -CF₃, F, CN and/or Cl as substituents or are incorporated into a 3- to 7-membered ring, in which, in addition, one or two non-adjacent CH₂ groups may be replaced by -O- and one CH₂ group non-adjacent to these groups may be replaced by -OC(=O)-;
- 15

X is a single bond, -O-, OC(=O)-, -C(=O)O- or -OC(=O)O-

Y is -OC(=O)-, -OCH₂-, -CH₂CH₂-

- 20 **A¹, A², A³** are each, independently of one another, phenylene-1,4-diyl, unsubstituted or monosubstituted or disubstituted by CN or F, phenylene-1,3-diyl, unsubstituted or monosubstituted or disubstituted by CN or F, cyclohexane-1,4-diyl, in which one or two H atoms may be replaced by CN and/or CH₃ and/or F, 1-cyclohexene-1,4-diyl, in
- 25 which one H atom may be replaced by F, 1-alkyl-1-silacyclohexane-1,4-diyl, pyridine-2,5-diyl, unsubstituted or monosubstituted by F, pyrimidine-2,5-diyl, unsubstituted or monosubstituted by F, cyclopentane-2,5-diyl or thiophene-2,5-diyl;

- 30 **M¹, M²** are undirected and are each, independently of one another, -OC(=O)-, -OCH₂-, -CH₂CH₂-, -OC(=O)CH₂CH₂-, -OCH₂CH₂CH₂-, -C≡C-, -CH₂CH₂CH₂CH₂- or a single bond;

a, b are each, independently of one another, 0 or 1.

2. A liquid-crystal mixture comprising at least one compound of the formula (I) as claimed in claim 1.

5

3. A liquid-crystal mixture as claimed in claim 2, which comprises from 0.01 to 80% by weight of one or more compounds of the formula (I).

10

4. A liquid-crystal mixture as claimed in claim 2 or 3, which is ferroelectric (chiral smectic).

5. A liquid-crystal mixture as claimed in claim 2 or 3, which is nematic.

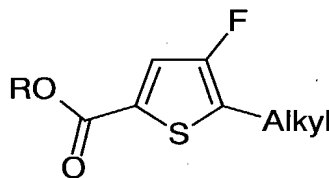
15

6. A ferroelectric switching and/or display device, which contains a ferroelectric liquid-crystal mixture as claimed in claim 4.

7. A ferroelectric switching and/or display device as claimed in claim 6, which contains active matrix elements and wherein the liquid-crystal layer forms a monostable monodomain.

20

8. A 5-alkyl-4-fluoro-thiophene-2-carboxylic acid of the formula (II)

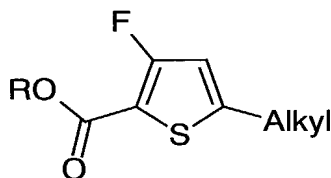


(II)

25

in which alkyl is a straight-chain or branched alkyl radical of 2 to 16 carbon atoms and R is hydrogen, alkali metal, alkaline earth metal (1/2), a straight-chain or branched alkyl radical of 1 to 16 atoms with the exception of methyl and tert-butyl, or a corresponding acid halide.

9. A 5-alkyl-3-fluoro-thiophene-2-carboxylic acid of the formula (III)



(III)

in which alkyl is a straight-chain or branched alkyl radical of 2 to 16 carbon atoms and R is hydrogen, alkali metal, alkaline earth metal (1/2), a straight-chain or branched alkyl radical of 1 to 16 atoms or a corresponding acid halide.

10. The use of compounds of the general formulae (II) and (III) as claimed in claims 8 and 9 for preparing liquid crystals, agrochemicals and pharmaceuticals.

11. A fluorinated five-membered ring compound as claimed in claim 1, wherein, in the cyclopentene derivatives (vi), T is 1-cyclopentene-1,3-diyl, 1-cyclopentene-1,4-diyl or 3-cyclopentene-1,3-diyl.

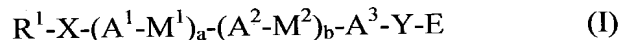
12. A fluorinated five-membered ring compound as claimed in claim 11, wherein, in the cyclopentene derivatives (vi), the moiety $-\text{Y}-\text{T}-$ is

1-cyclopentene-1-carbonyloxy-3-yl, 1-cyclopentene-1-carbonyloxy-4-yl or 3-cyclopentene-1-carbonyloxy-3-yl.

Abstract

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Fluorinated five-membered ring compounds of the formula (I)



10 where **E** is a radical $T-Z-R^2$ containing a five-membered ring and, for example,

T is undirected and is 4-fluorothiophene-2,5-diyl, 3-fluorothiophene-2,5-diyl,
3-fluorothiophene-2,4-diyl, 5-fluorothiophene-2,4-diyl, furan-2,5-diyl,
furan-2,4-diyl, isoxazole-3,5-diyl, thiazole-2,5-diyl, thiazole-2,4-diyl,
15 cyclopentane-1,3-diyl or cyclopentene-1,3-diyl,

R¹ and **R²** are hydrogen,

X is a single bond, -O-, OC(=O)-, -C(=O)O- or -OC(=O)O-,

20 **Y** is -OC(=O)-, -OCH₂-, -CH₂CH₂-,

Z is a single bond or -O-,

A¹, **A²**, **A³** are each, independently of one another, phenylene-1,4-diyl,

25 **M¹**, **M²** are undirected and are each, independently of one another,

-OC(=O)-, -OCH₂-, -CH₂CH₂-, -OC(=O)CH₂CH₂-, -OCH₂CH₂CH₂-,

-C≡C-, -CH₂CH₂CH₂CH₂- or a single bond,

a, **b** are each, independently of one another, 0 or 1,

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are used in FLC mixtures.

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DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes reference to PCT International Applications)

FROMMER LAWRENCE & HAUG, LLP
File No.: 514453-3916

As a below named inventor, we hereby declare that:

Our residences, post office addresses and citizenships are as stated below next to our names.

We believe we are original, first and joint inventors (if plural, names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention ENTITLED:

FIVE MEMBERED-RING COMPOUNDS AND UTILIZATION THEREOF IN LIQUID CRYSTAL MIXTURES

the specification of which:

- is attached hereto
- X was filed on February 27, 2002 as:
 - X United States Application Serial No. 10/070242
 - X Corresponding to International Appln. No. **PCT/EP00/08518** filed **August 31, 2000** with amendments through DATE EVEN HEREWITH (if applicable, give details).

We hereby state that we have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to our to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

We hereby claim foreign priority benefits under Title 35, United States Code § 119 (a) - (d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365 (a) of any PCT International application(s) designating at least one country other than the United State of America listed below and have also identified below any foreign application for patent or inventor's certificate or any PCT International applications designating at least one country other than the United States of America filed by us on the same subject matter having a filing date before that of the application(s) on which priority is claimed: Prior Foreign/PCT Application(s) [list additional applications on separate page]:

Country (or PCT)	Application Number:	Filed (Day/Month/Year)	Priority Claimed:	
			Yes	No
Germany	199 41 649.4	September 1, 1999	x	
Germany	199 41 651.6	September 1, 1999	x	
Germany	199 41 650.8	September 1, 1999	x	
Germany	199 41 653.2	September 1, 1999	x	
Germany	199 41 654.0	September 1, 1999	x	
Germany	199 41 656.7	September 1, 1999	x	

We hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

We hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s) or § 365 (c) of any PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior United States or PCT International application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, we acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to us to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Prior U.S. (or U.S.-designating PCT) Application(s) [list additional applications on separate page]:

U.S. Serial No.:	Filed (Day/Month/Year)	PCT Application No.	Status (patented, pending, abandoned)
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✓ We hereby appoint William F. Lawrence, Registration No. 28,029, and FROMMER LAWRENCE & HAUG, LLP or their duly appointed associates, our attorneys or agents, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to file continuation and divisional applications thereof, to receive the Patent, and to transact all business in the Patent and Trademark Office and in the Courts in connection therewith, and to insert the Serial

Number of the application in the space provided above, and specify that all communications about the application are to be directed to the following correspondence address:

William F. Lawrence, Esq.
c/o FROMMER LAWRENCE &
HAUG, LLP
745 Fifth Avenue
New York, NY 10151

Direct all telephone calls to: (212) 588-0800
to the attention of:
William F. Lawrence
FAX (212) 588-0500

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Post Office Address(es) of inventors [if different from residence]:

NOTE: In order to qualify for reduced fees available to Small Entities, each inventor and any other individual or entity having rights to the invention must also sign an appropriate separate "Verified Statement (Declaration) Claiming [or Supporting a Claim by Another for] Small Entity Status" form [e.g. for Independent Inventor, Small Business Concern, Nonprofit Organization, Individual Non-Inventor].